

METHOD AND APPARATUS TO PROVIDE REDUCTANT FOR NO_x

BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates to abatement of pollutants and, in particular, to an apparatus for the reduction of nitrogen oxides in a gas stream, a method for producing reductant for use in reducing nitrogen oxides and a method for operating an apparatus for the reduction of nitrogen oxides.

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Related Art

It is well-known that the exhaust of diesel engines contains noxious pollutants including carbon monoxide ("CO"), unburned hydrocarbons ("HC") and nitrogen oxides ("NO_x"). It is common practice to provide engine systems with abatement means comprising catalysts
15 designed to convert these noxious pollutants into relatively innocuous species such as carbon dioxide, water and nitrogen. Such catalysts are well-known and may comprise oxidation catalysts to oxidize CO and HC to CO₂ and H₂O and reduction catalysts to reduce NO_x to nitrogen. Separate reduction and oxidation catalysts may be placed in the exhaust gas discharge line in series, or a "three-way conversion" catalyst may be used, for the substantially
20 simultaneous oxidation of HC and CO and reduction of NO_x. Many catalytic materials are well-known for such purposes, for example, catalytic components that may comprise one or more platinum group metals such as platinum, palladium and rhodium, dispersed on a typically inert support material that may comprise a high surface area support such as a predominantly gamma-alumina support. The catalytic material may contain other components such as ceria
25 and/or other base metal oxides as well as various other stabilizers and promoters. As is well-known in the art, such catalytic materials may be coated as a washcoat onto the walls of the gas flow passages of a refractory support, such as stainless steel or ceramic-like support, e.g., a cordierite support having a plurality of fine, parallel gas flow passages extending therethrough to provide a flow-through catalyst member. The abatement means may comprise a particulate
30 trap for removing particulates from the exhaust gas stream and/or an adsorbent material. Catalysts may be used in conjunction with other abatement means, as is known in the art.

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One known expedient in the art for improving catalytic NO_x conversion is to directly inject diesel fuel into the catalyst bed as a reductant during lean engine operating conditions. However, when diesel fuel is injected into a cold catalyst, i.e., at a temperature lower than about 200°C, and/or when the exhaust gas temperature is lower than the vaporization temperature of the fuel, the efficiency and functionality of the catalyst for the reduction of NO_x is significantly reduced.

Japanese Patent 92JP-258044 of Kumagai et al for "Exhaust Emission Control Device" pertains to a NO_x-reducing catalyst mounted in an exhaust pipe. The NO_x-reducing catalyst is activated by a reducing agent (i.e., hydrocarbons). Liquid hydrocarbon fuel drawn from a fuel tank is contacted with a reforming catalyst which produces low molecular weight liquid hydrocarbon that is injected into the exhaust gas stream via an injector positioned upstream from the NO_x-reducing catalyst. This reference does not show the addition of oxygen to the reducing agent.

U.S. Patent 5,357,908 to Sung et al, dated October 25, 1994, discloses a fuel modification method and apparatus in which fuel vapors and/or liquid fuel without added oxygen are cracked by cracking catalyst bed (30) before being provided to the engine. The distillate (i.e., the cracked fuel) is used during the engine cold start period to improve (i.e., lower) the light-off activity temperature of the catalyst. The cracking catalyst bed (30) can be regenerated by flowing oxygen therethrough to burn off carbonaceous deposits and flowing the effluent into the exhaust treatment apparatus at a point upstream of the catalytic converter (22). The hydrocarbon fuel is directed away from the cracking catalyst bed during regeneration (see column 8, lines 44-50).

U.S. Patent 3,896,616 to Keith et al, dated July 29, 1975, discloses an exhaust gas treatment apparatus including an initial or warm-up catalyst and a downstream catalyst. During fuel-rich cold-start operation, oxygen is added to the exhaust gas by adding air at a point upstream from the warm-up catalyst so that it can oxidize the unburned hydrocarbons therein (see column 4, lines 3-23). The effect of adding the air under these conditions is to lower the light-off temperature of the catalyst. After the warm-up period, the warm-up catalyst is then used to reduce NO_x in the gas stream and for this purpose, additional fuel is added to the exhaust gas (see column 4, lines 24-43). The Patent discloses the preference for the use of hydrocarbon fuel reductant in the C-3 to C-12 range (see column 8, line 65 through column 9, line 3).

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In describing engine operating conditions and the composition of exhaust gases resulting therefrom, references to "rich" and "lean" operation or exhaust gases refer to the proportion of air to fuel provided to the engine and, by extension, to the proportion of unconsumed oxygen to unburned hydrocarbons in the exhaust gas. An air-fuel ratio of 14.65 (wt. basis) is the stoichiometric ratio corresponding to the combustion of a hydrocarbon fuel with an average formula $\text{CH}_{1.88}$. Fuels with different carbon/hydrogen ratios will require slightly different air-fuel ratios to produce a stoichiometric mixture. To avoid confusion in making comparisons, the Greek symbol λ has been used at times to represent the relationship of a particular air-fuel ratio to the stoichiometric ratio. The air-fuel ratio is divided by the stoichiometric ratio so that in this system $\lambda = 1$ is a stoichiometric mixture. $\lambda > 1$ is a fuel-lean mixture and $\lambda < 1$ is a fuel-rich mixture. For example, at an air-fuel ratio of 14.5, the $\lambda = 14.5/14.65 = 0.9898$.

SUMMARY OF THE INVENTION

The present invention provides an apparatus effective for generating activated reductant from a source hydrocarbon. The apparatus comprises a mixer for receiving and mixing a source hydrocarbon and oxygen and activation means for speciating the source hydrocarbon to produce activated reductant.

In one embodiment, the apparatus may comprise a mixer having inlets for receiving the source hydrocarbon and oxygen, a mixing chamber for creating a mixture of the source hydrocarbon and oxygen and an outlet for discharging activated hydrocarbon species, and also a catalyst disposed in the mixer for contact with the mixture, the catalyst being effective for activating the source hydrocarbon.

According to one aspect of the invention, the apparatus may comprise a glow plug comprising a catalyzed heating element disposed in the mixer.

In another embodiment, an apparatus according to the present invention comprises a mixer having inlets for receiving the source hydrocarbon and oxygen, a mixing chamber for creating a mixture of the source hydrocarbon and oxygen and an outlet, and also a heating element positioned to generate activated hydrocarbons from the mixture of the source hydrocarbon and oxygen. Optionally, the heating element may be disposed in the mixing chamber. In a particular embodiment, the heating element may comprise a glow plug mounted thereon with the heating element in the mixing chamber. Additionally or alternatively, a heating element may be positioned to contact the mixture discharged from the outlet of the

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mixer to generate activated hydrocarbon species therefrom. For example, the heating element may have a heater inlet connected to the mixer outlet for receiving the mixture of source hydrocarbon and oxygen and a heater outlet for discharging activated hydrocarbon species. There may be a catalyst in the heating element positioned to contact the mixture prior to
5 discharge of the activated hydrocarbon species from the heater outlet.

An apparatus according to the present invention may further comprise a temperature sensor for sensing the temperature of a gas stream and an oxygen sensor for sensing whether such gas stream is lean, and may further comprise a control unit responsive to the sensors, for initiating the apparatus when the oxygen sensor indicates a lean gas stream and the temperature
10 sensor indicates a temperature of less than 200°C. The control unit may be configured to initiate the apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C. There may be an air pump connected for delivering oxygen to the mixer and a fuel pump connected for delivering source hydrocarbon to the mixer.

According to one aspect of the invention, the apparatus may further comprise a
15 temperature sensor for sensing the temperature of the gas stream and an oxygen sensor for sensing whether the gas stream is lean. There may also be a control unit responsive to the sensors, for initiating the apparatus when the oxygen sensor indicates a lean gas stream and the temperature sensor indicates a temperature of less than 200°C, e.g., a temperature in the range of about 140°C to 160°C, wherein activating the apparatus comprises activating the air pump
20 and the fuel pump.

The present invention also provides an apparatus effective at least for the reduction of oxides of nitrogen (NO_x) in a gas stream, the apparatus comprising a supply of source hydrocarbon, a source of oxygen, an apparatus effective for generating activated reductant as described above, and a NO_x -reduction catalyst positioned for contact with the gas stream with
25 the activated reductant therein.

The present invention also provides a method for producing an activated hydrocarbon species, comprising mixing a source hydrocarbon with oxygen and subjecting the mixture to activating conditions. In a particular embodiment of this method, the source hydrocarbon may comprise diesel fuel.

30 The method may comprise contacting the mixture with a catalytic material effective to facilitate speciation of the source hydrocarbon. It may comprise heating the mixture to a temperature of at least about 350°C, optionally without a catalyst, or contacting the mixture at a

temperature lower than 350°C, e.g., in the range of from about 200°C to 340°C, and contacting the mixture with a catalyst effective to facilitate speciation at such lower temperature.

The present invention also provides an activated hydrocarbon reductant produced by the method comprising mixing a source hydrocarbon with oxygen and subjecting the mixture to
5 activating conditions. In a particular embodiment, the source hydrocarbon may comprise diesel fuel.

The invention also relates to a method for reducing oxides of nitrogen (NO_x) in a lean gas stream. The method comprises creating a fuel-oxygen mixture by mixing diesel fuel vapor with oxygen, subjecting the fuel-oxygen mixture to activating conditions to create an activated
10 diesel reductant, mixing the activated diesel reductant into the gas stream and contacting the gas stream with the activated diesel reductant therein with a NO_x-reduction catalyst. The method may comprise mixing the activated diesel reductant with the gas stream at a temperature below 200°C, e.g., at a temperature in the range of about 140°C to 200°C or in the range of about 140°C to 160°C.

Furthermore, this invention provides a method of operating an apparatus for the
15 reduction of NO_x in a lean gas stream. This method comprises flowing the gas stream into contact with a NO_x-reduction catalyst, sensing the temperature of the gas stream contacting the NO_x-reduction catalyst and introducing activated diesel reductant into the gas stream for contact with the NO_x-reduction catalyst when the temperature of the gas stream is in the range of 140°C
20 to 200°C, e.g., in the range of 140°C to 160°C.

This invention also presents an improved glow plug comprising a heating element extending from a plug body, the improvement comprising that a coating of catalytic material is carried on the heating element, the catalytic material being effective to facilitate the speciation of a source hydrocarbon. There may be an anchor layer on the heating element between the
25 heating element and the catalytic material, and the anchor layer may comprise a metal that is thermally sprayed onto the heating element of the glow plug. For example, the anchor layer may be electric arc sprayed onto the heating element of the glow plug. The anchor layer may be deposited on the heating element by electric arc spraying a metal feedstock selected from the group consisting of nickel, Ni/Al, Ni/Cr, Ni/Cr/Al/Y, Co/Cr, Co/Cr/Al/Y, Co/Ni/Cr/Al/Y,
30 Fe/Al, Fe/Cr, Fe/Cr/Al, Fe/Cr/Al/Y, Fe/Ni/Al, Fe/Ni/Cr, 300 series stainless steels, 400 series stainless steels, and mixtures of two or more thereof. In a particular embodiment, the anchor layer may comprise nickel and aluminum. Optionally, the aluminum may comprise from about

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3 to 10 percent, e.g., from about 4 to 6 percent, of the combined weights of nickel and aluminum in the anchor layer. Typically, the catalytic material is deposited on the anchor layer and may comprise a refractory metal oxide support on which one or more catalytic metal components are dispersed.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1A, 1B, 1C, 2 and 3A and 3B are chromatogram plots of molecular weight distributions of hydrocarbon species in diesel fuel vapor samples, generated by a gas chromatograph analyzer;

10 Figure 4 is a schematic diagram of a typical diesel engine system including an exhaust treatment apparatus in accordance with the present invention; and

Figures 5A, 5B, 6, 7A and 7B are schematic diagrams showing various embodiments of exhaust treatment apparatuses in accordance with the present invention.

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DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS THEREOF

The present invention relates to abatement of pollutants and, in particular, to an apparatus for the reduction of nitrogen oxides in a gas stream, a method for producing reductant for use in reducing nitrogen oxides and a method for operating an apparatus for the reduction of
20 nitrogen oxides. The invention is especially pertinent to the reduction of NO_x from lean exhaust gases. The present invention provides for the activation of a source hydrocarbon to provide a reductant, referred to herein and in the claims as "activated reductant", that is more reactive as a reductant for the NO_x than the source hydrocarbon. The superior activity of activated reductant relative to the source hydrocarbon is believed to be due to the generation from the source
25 hydrocarbon of lower molecular weight hydrocarbon species which render the fuel vapors more reactive than the source hydrocarbon. For this reason, activation of the source hydrocarbon is also sometimes referred to herein as "speciation" or "cracking" of the source hydrocarbon. In particular embodiments of the present invention, the source hydrocarbon comprises diesel fuel and the activated reductant is sometimes referred to herein as "activated diesel reductant",
30 which is believed to contain a significant proportion of low molecular weight hydrocarbon species, e.g., C-10 or smaller (e.g., C-3, C-4).

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The use of activated reductant permits the effective use of the catalyst for the reduction of NO_x at temperatures lower than those permitted by the source hydrocarbon. When the reductant is non-activated diesel fuel vapor, the effectiveness threshold temperature for a conventional lean NO_x -reduction catalyst is about 200°C . Below the threshold temperature, the reduction reaction is inadequate and the non-activated diesel fuel vapors condense on the catalyst and deactivate it. The use of activated diesel reductant facilitates the reduction reaction, lowering the effectiveness threshold temperature below 200°C , e.g., from about 140°C to 200°C and/or from about 140°C to 160°C . In addition, the activated diesel reductant, being of lower molecular weight and therefore generally more volatile than non-activated diesel fuel vapors, does not exhibit a condensation problem at those temperatures as does the source hydrocarbon. Naturally, the present invention may optionally be practiced at the temperature range in which non-activated reductant is acceptable as well, i.e., at 200°C or higher.

One feature of the invention relates to the Applicants' finding that speciation is greatly facilitated when a source hydrocarbon, e.g., diesel fuel vapor, is mixed with a limited amount of oxygen and the mixture is exposed to activating conditions, presumably because the source hydrocarbon is partially oxidized as it is cracked into hydrocarbons of lesser molecular weight. The oxygen may be included in air mixed with the fuel or may be provided from any other suitable source. Preferably, the proportion of oxygen in the mixture relative to the quantity of carbon atoms corresponds to an $\text{O}_2:\text{C}$ ratio of at least about 0.3:1 (i.e., an oxygen-to-carbon atomic ratio in the mixture of at least about 0.6:1), since it is believed that lesser amounts of oxygen will lead to coking of the source hydrocarbon that will foul the apparatus. It is believed that a loss of efficiency in the production of light hydrocarbons (excluding CO_2) is exhibited as the ratio increases above 0.5:1, which is a preferred $\text{O}_2:\text{C}$ ratio, but acceptable production of light hydrocarbons can be obtained up to an $\text{O}_2:\text{C}$ ratio of about 0.8:1. Practical working ranges for the $\text{O}_2:\text{C}$ ratio include ratios in the range of from about 0.3:1 to 0.6:1, from about 0.35:1 to 0.5:1, from about 0.35:1 to 0.45:1, and from about 0.42:1 to 0.5:1.

In accordance with this invention, the oxygen-hydrocarbon mixture is subjected to activating conditions, which includes heating the mixture to a speciation temperature, i.e., a temperature at which speciation, e.g., partial oxidation, occurs. The speciation temperature may be at least about 350°C in the absence of a catalyst, but may be lower than 350°C when subjecting the mixture to activating conditions includes contacting the mixture with a catalyst effective to facilitate speciation of the fuel, i.e., a speciation catalyst. The speciation catalyst

may comprise a partial oxidation catalyst, i.e., a catalyst that facilitates the partial oxidation of the source hydrocarbon. In the presence of such a catalyst, the speciation temperature may be as low as about 200°C, i.e., speciation may occur at temperatures of 200°C or greater, e.g., at temperatures of from about 200°C to 350°C, e.g., from about 200°C to 340°C or from about
5 200°C to 300°C.

Another feature of the invention relates to hydrocarbon activation apparatuses or activated reductant means for mixing a source hydrocarbon such as diesel fuel with oxygen and speciating the source hydrocarbon by subjecting the mixture to activating conditions to produce an activated reductant. Such an apparatus is preferably configured for use as an exhaust
10 treatment apparatus through which an exhaust gas stream flows for treatment. The oxygen-source hydrocarbon mixture may be activated either before or after it is provided to the exhaust gas stream. For example, the activated reductant means may include a mixer such as a fuel injector for mixing the source hydrocarbon with oxygen. The activated reductant means may comprise an activating means such as a heat source for heating and/or vaporizing the source
15 hydrocarbon and/or otherwise heating the oxygen-hydrocarbon mixture in any manner effective to raise the temperature of the mixture to a speciation temperature. The heat source may comprise, e.g., an electric heating element or a glow plug. Alternatively, or in addition to the heat source, the activating means may comprise a catalyst that facilitates the activation of the reductant by catalyzing or facilitating speciation of the source hydrocarbon. For example, a
20 catalyst member comprising a carrier coated with catalytic material can be mounted in the injector or for contact with the oxygen-hydrocarbon mixture created therein. There may be a heat source for heating the catalyst, e.g., there may be a heating element for heating a catalytic material, e.g., for heating a catalyst member. In a particular embodiment, the activating means may comprise a catalyzed glow plug.

25 According to particular embodiments of the invention in which the NO_x is present in the exhaust gas stream of a diesel engine and wherein the source hydrocarbon comprises diesel fuel, an exhaust gas treatment apparatus may comprise an activated reductant means comprising a fuel injector connected to an exhaust pipe for the engine, for mixing the fuel with oxygen. There may be a coupling fixture or holder to couple the fuel injector to the exhaust pipe and to
30 accommodate activating means such as a heating element and/or a catalyst to facilitate speciation of the fuel exiting the injector before it enters the exhaust pipe. Alternatively, the injector may be modified to accommodate the activating means. In yet another embodiment, a

conventional injector can be used to form the oxygen-diesel fuel mixture and inject it into the exhaust gas pipe, and the exhaust pipe may be modified to accommodate the activating means and to flow the mixture into contact therewith. Optionally, the mixture may be isolated from the exhaust gas until after the reductant is activated, e.g., by means of a conduit within the exhaust pipe within which the activating means is disposed and through which the mixture flows to contact the activating means, after which it leaves the conduit and is mixed with the exhaust gas. By disposing the activating means in a holder for the injector and/or within the exhaust gas pipe and/or within the injector itself, the Applicants have provided a means for activating the reductant without adding significantly to the spatial demands of a conventional NO_x abatement system or a conventional exhaust gas treatment apparatus.

The Applicants performed experiments using a gas chromatograph ("gc") to determine conditions that favor "activation" or "speciation" of diesel fuel vapor hydrocarbons and that can be replicated using the activated reductant means described herein. In these experiments, a 1 centimeter (cm) x 2.5 cm inert catalyst carrier core was loaded into a portable reactor that was attached to the front of a gas chromatograph with graphite ferrules. In some tests the carrier core was uncoated; in others, the core carried a washcoat of a catalytic material effective to facilitate speciation of the fuel, i.e., to facilitate catalytic partial oxidation (CPO); and in still others the CPO material was tested in powder form.

In a typical test procedure, the reactor and all the interface lines were stabilized at 300°C for at least 1 hour. In various trials, helium or zero grade air at 10 psi was introduced into the injection system in front of the reactor. In each test, a 10 microliter aliquot of No. 2 diesel fuel was injected through a septum into the flowing helium or air at a point upstream from the carrier core. The helium or air supply was turned off after a 12 second injection. The space velocity through the carrier core was typically in the range of 250 to 500 hr⁻¹. A gc analysis was performed on the effluent from the uncoated or coated carrier core. The formation of "activated" reductant was observed as the detection of an increase in the proportion of lightweight hydrocarbons, i.e., C-10 or less, preferably C-3 and C-4, in the sample, some of which may have been oxygenated (i.e., in the form of alcohols, aldehydes, etc.).

Some tests were performed using an uncoated or "blank" carrier core and helium. The results of these tests showed that heating diesel fuel vapors in an inert atmosphere, e.g., in mixture with helium, did not cause significant speciation, i.e., activation, of the diesel fuel hydrocarbons, i.e., there was no significant increase in the proportion of lightweight

hydrocarbons, even when heated to temperatures as high as 475°C. However, the Applicants have found that when diesel fuel vapors are mixed with limited amounts of oxygen, which may be supplied by air or any other suitable source, speciation can be induced by exposing the mixture to activating conditions. The diesel fuel reductant thus becomes "activated", i.e., a significant portion of the diesel fuel is converted into lightweight hydrocarbon species, i.e., C-10 or less. Activating conditions have been found to include heating the mixture to a temperature of at least about 350°C in the absence of a catalyst. Activating conditions also include contacting the oxygen-fuel mixture with a catalytic material effective to facilitate speciation, e.g., the catalytic partial oxidation ("CPO"), at temperatures that may optionally be lower than 350°C but typically at least about 200°C. Materials suitable for use as CPO catalytic materials are described below.

To illustrate the findings and results realized in accordance with the present invention, the chromatogram of Figure 1A shows the results of a gas chromatograph analysis of vaporized diesel fuel that was mixed with helium (an inert gas) instead of oxygen, heated to 350°C and flowed through a blank core, while Figure 1B shows the results obtained when vaporized diesel fuel and helium with no added oxygen were flowed over a catalyst at 450°C. In these Figures and in Figures 1C, 2, 3A and 3B, the horizontal axis indicates retention time (in minutes) and the vertical axis indicates a response voltage (in millivolts) derived from a detector, as is well-known in the art. Figures 1A and 1B show that no significant cracking or speciation occurs in an inert atmosphere in the absence of a catalyst, even at high temperature. These results show that the disclosure of Japanese patent document 92JP-258044 discussed above is not enabling with respect to the generation of activated hydrocarbon reductant from a diesel fuel source hydrocarbon.

Figure 1C shows the results of a mixture of the vaporized diesel fuel with air (as a source of oxygen) heated to 340°C and flowed through a blank core. The outcome was similar to that of Figures 1A and 1B, and indicates that even in the presence of air, a temperature of 340°C is not adequate to generate significant speciation in the absence of a catalyst.

Figure 2 presents the non-catalytic, thermal cracking results obtained by flowing the air-fuel mixture over a blank core at 350°C, and shows by virtue of the reduced spikes in the 5 minute to 20 minute range and the strong spike at about two minutes that a significant proportion of the diesel fuel hydrocarbons were cracked into lightweight species.

Test data obtained from the air-fuel mixture revealed that at temperatures below 350°C, the proportion of light hydrocarbons (smaller than C-10) in the effluent, excluding carbon dioxide, was in the range of 0.3 to 0.4 percent. As the temperature rises from 350°C to 450°C, the proportion of light hydrocarbons (HC) increases as

5 shown in the following TABLE I.

TABLE I

Air-Fuel Mixture		% Light HC (<C-10)
<u>Injector Temperature °C</u>		<u>(Excluding CO₂)</u>
10	300	0.4%
	325	0.4%
	340	0.3%
	340	0.3%
	345	0.3%
15	350	5.7%
	350	5.8%
	375	26.8%
	400	34.7%
	450	36.2%

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The data of TABLE I illustrate that significant speciation occurs in an air-fuel mixture at temperatures of at least about 350°C, with a significant increase between 350°C and 375°C.

Other gc tests show that the use of a CPO catalyst facilitates speciation at temperatures lower than that required for non-catalytic speciation, i.e., lower than 350°C, e.g., to 300°C. In these tests, catalysts were used in two forms; in powder form, in which case the air-fuel mixture was flowed through a powder reactor having a volume of about 0.125 cubic centimeters (cc) and containing about 100 milligrams of catalytic material powder, and in the form of a coating on the catalyst carrier core having a one centimeter (cm) diameter and a volume of about 1.96 cc at a coating weight of about 1.8 grams/cc.

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A variety of catalytic components was found to be effective for use in CPO catalytic materials, including supported precious metals, rare earth metal compounds, transition metal compounds and zeolite-based materials, and these will generally be effective either alone or in

combination. The following Examples present data obtained from the use of supported precious metal-type catalysts, specifically, catalytic materials comprising a catalytic component comprising rhodium dispersed on alumina. It will be understood by one of ordinary skill in the art, however, that other supported catalytic components, e.g., other platinum group metals, may be used effectively in this way, and that they may be supported on any of a variety of refractory inorganic oxide support materials.

CPO catalytic materials comprising supported catalytic components can be prepared by procedures well known in the art, e.g., by dispersing a compound and/or complex of any catalytically active component, e.g., one or more platinum group metal compounds or complexes, onto a relatively inert bulk support material. The compounds or complexes of one or more catalytic components may be dissolved or suspended in any liquid which will wet or impregnate the support material, which does not adversely react with other components of the catalytic material and which is capable of being removed from the catalyst by volatilization or decomposition upon heating and/or the application of a vacuum. Generally, both from the point of view of economics and environmental aspects, aqueous solutions of soluble compounds or complexes are preferred. For example, suitable water-soluble platinum group metal compounds are chloroplatinic acid, amine solubilized platinum hydroxide, rhodium chloride, rhodium nitrate, hexamine rhodium chloride, palladium nitrate or palladium chloride, etc. The compound-containing liquid is impregnated into the pores of the bulk support particles of the catalyst, and the impregnated material is dried and preferably calcined to remove the liquid and bind the platinum group metal into the support material. In some cases, the completion of removal of the liquid (which may be present as, e.g., water of crystallization) may not occur until the catalyst is placed into use and subjected to the high temperature exhaust gas. During the calcination step, or at least during the initial phase of use of the catalyst, such compounds are converted into a catalytically active form of the platinum group metal or a compound thereof. An analogous approach can be taken to incorporate the other components into the catalytic material. Optionally, the inert support materials may be omitted and the catalytic material may consist essentially of the catalytic component deposited directly on the sprayed carrier substrate by conventional methods.

Suitable support materials for the catalytic component include alumina, silica, titania, silica-alumina, aluminosilicates, aluminum-zirconium oxide, aluminum-chromium oxide, etc. Such materials are preferably used in their high surface area forms. For example, gamma-

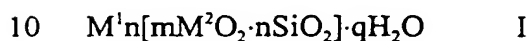
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alumina is preferred over alpha-alumina. It is known to stabilize high surface area support materials by impregnating the material with a stabilizer species. For example, gamma-alumina can be stabilized against thermal degradation by impregnating the material with a solution of a cerium compound and then calcining the impregnated material to remove the solvent and
5 convert the cerium compound to a cerium oxide. The stabilizing species may be present in an amount of from about, e.g., 5 percent by weight of the support material.

As is known in the art, modifiers may optionally be employed in activated-alumina containing catalyst compositions. Among such modifiers are thermal stabilizers which serve to retard undesirable alumina phase transitions (e.g., gamma- to alpha-alumina) at elevated
10 temperatures which the catalyst may encounter in use. The thermal stabilizers may be any known stabilizer or combination of stabilizers such as, for example, one or more rare earth metal oxides, silicon dioxide, oxides of Group IVB metals (zirconium, hafnium and titanium) or one or more alkaline earth metal oxides. Other modifiers such as oxides of chromium, iron and nickel, or their precursors, may also be employed. Some modifiers may serve more than one
15 function, e.g., may serve as both a thermal stabilizer and a catalytic promoter. These materials, or precursors thereof, may be impregnated from a solution or liquid dispersion into the activated alumina particles either before or after the particles are formed into an adherent coating on the carrier substrate. (As used herein and in the claims, a "precursor", whether of a thermal stabilizer, other modifier or other component, is a compound, complex or the like which, upon
20 calcining or upon use of the catalyst, will decompose or otherwise be converted into, respectively, a thermal stabilizer, other modifier or component.) The presence of one or more of these metal oxide stabilizers tends to retard the phase transition of high surface area aluminas such as gamma- and eta-alumina to alpha-alumina, which is a low surface area alumina. The retardation of such phase transformation tends to prevent or reduce the occlusion of the catalytic
25 metal component by the alumina with the consequent decrease of catalytic activity. The amount of metal oxide stabilizer combined with the alumina may be from about 0.05 to 30 weight percent, preferably from about 0.1 to 25 weight percent, based on the total weight of the combined alumina, stabilizer and catalytic component. Alkaline earth metal oxides which may be used to stabilize activated alumina are oxides of barium, strontium, calcium and magnesium.
30 Among the rare earth metal oxides which may be similarly employed in the catalyst are oxides of cerium, lanthanum, neodymium, praseodymium and mixtures thereof, including the commercially available mixtures of rare earth metal oxides.

The zeolitic catalysts that may be used as CPO catalysts in the practice of this invention may be of the type that have cracking properties for long-chain and aromatic hydrocarbons, and so may crack long-chain hydrocarbons in the reductant.

Zeolites that are known to be useful for cracking long-chain hydrocarbons include the following structural types: faujasites, pentasiles, mordenites, ZSM 12, zeolite β , zeolite L, zeolite Ω , ZSM 22, ZSM 23, ZSM 48, EU-1 and the like. The zeolite of the pentasile type may exhibit a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 25 to 2,000, e.g., between 40 and 600. Zeolites are crystalline aluminosilicates which are made up of a network of SiO_4 or M^2O_4 tetrahedrons and may be characterized by the general formula (I)



wherein

M^1 is an equivalent of an exchangeable cation, its quantity corresponding to the M^2 quantity;

M^2 is a trivalent element which together with the Is forms the oxidic framework of the zeolite;

n/m is the $\text{SiO}_2/\text{M}^2\text{O}_2$ ratio;

q is the amount of adsorbed water.

The individual tetrahedrons are linked at the apices of the tetrahedrons via oxygen bonds and form a three-dimensional network which is regularly traversed by channels and hollow spaces. Various zeolite structures differ in their arrangement and size of the channels and hollow spaces and in their compositions. As a counterbalance of the negative charge of a zeolite lattice, which is accounted for by the M^2 content, exchangeable cations are deposited. The adsorbed aqueous phase qH_2O is reversibly removable without the framework losing its structure.

M^2 is often aluminum but can be partially or completely substituted by other trivalent elements.

A detailed description of zeolites is given, e.g., in the monograph by D.W. Breck *"Zeolite Molecular Sieves, Structure, Chemistry and Use"*, J. Wiley & Sons, New York, 1974.

A further description, in particular of the SiO_2 -rich zeolites which are of interest for catalytic uses, is given in the monograph by P.A. Jacobs and J.A. Martens *"Synthesis of High-Silica*

Aluminosilicate Zeolite", Studies in Surface Science and Catalysis, Vol. 33, Ed. B. Delmon and J.T. Yates, Elsevier, Amsterdam-Oxford-New York-Tokyo, 1987.

Some zeolites of the kind described above are disclosed in European Patent Application 92 10 2161.4(A1). In the zeolites described therein, M^2 is one or several elements from the group Al, B, Ga, In, Fe, Cr, V, As and Sb, preferably one or several elements of the group Al, B, Ga and Fe. It is further taught that the aforementioned zeolites could contain Li, Na, K, Rb, Cd, Cs, Mg, Ca, Sr, Ba and the transition metal cations such as B, Cr, Mn, Fe, Co, Ni, Cu, V, Nb, Mo, Ru, Rh, Pd, Ag, Ta, W, Zn, Re, Pt as exchangeable cations M^1 . Similarly useful are cations of the rare earth group and protons. Zeolites in which at least part of the metal cations, preferably 50-100% thereof, have been replaced by hydrogen ions (H^+), i.e., acid zeolites, are preferred. It is particularly preferred that 80-100% of all metal cations originally present be replaced by H^+ .

The acidic H^+ forms of the zeolites may be obtained by exchanging ammonium ions for metal ions and by calcination of the thus exchanged zeolites. Repetition of the exchange procedure and subsequent calcination under the defined conditions leads to so-called ultrastable zeolites in the zeolites of the faujasite type which become thermically and hydrothermally more stable by this dealumination process. A further possibility to obtain SiO_2 -rich zeolites of the faujasite type is to specifically treat the water-free zeolites with $SiCl_4$ at elevated temperatures ($\geq 150^\circ C$). Aluminum is removed and at the same time silicon is introduced into the lattice. Treatment with ammonium hexafluorosilicate under certain conditions also results in SiO_2 -rich faujasites.

A further possibility for the exchange of protons in the case of zeolites that exhibit a SiO_2/Al_2O_3 ratio of at least 5:1 is to carry out the process with mineral acids.

It is known that the ion exchange with trivalent rare earth metal ions, individually and/or in admixture which preferably can be rich in lanthanum or cerium, leads to acidic centers, particularly in the case of faujasites, and that an exchange of aluminum for transition metal cations leads to acidic centers.

The above-described zeolites with acidic centers have the catalytic property of cracking hydrocarbons, i.e., of cleaving them into smaller fragments.

For purposes of the following Examples, CPO catalysts comprising rhodium dispersed on alumina were prepared. Typically, alumina powder having a surface area of about 90 square meters per gram was impregnated with a rhodium nitrate solution to 80 percent of incipient

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wetness. The rhodium nitrate solution was diluted to give a desired metal concentration by weight of rhodium plus alumina. The impregnated powder was milled with acetic acid in an amount of about 2 percent by weight of the material to produce a slurry. No other catalytically active species were added to the alumina. For purposes of some of the following tests, the slurry was coated onto the catalyst carrier core, which was then dried and calcined. In other tests, the slurry was simply dried and calcined for use in powder form in a powder reactor. In tests of exhaust gas treatment apparatuses demonstrating the present invention, the slurry was coated onto a catalyst carrier core or onto the surface of a glow plug, as appropriate.

Figures 3A and 3B show results obtained when a fuel-air mixture was flowed at 300°C through catalyst carrier cores coated with the rhodium-on-alumina catalyst material described above. Figure 3A shows the results obtained using the 0.3 weight percent rhodium catalytic material while Figure 3B shows the results obtained using the 3 percent rhodium catalytic material. Both Figures 3A and 3B show that significant speciation of the diesel fuel occurred.

A comparison of results obtained by using a catalytic material as a coating on a carrier core as opposed to being tested in powder form is provided in the following TABLE II.

TABLE II

Catalytic			
<u>Material</u>	<u>Form</u>	<u>% Light HC</u>	
3% Rh/alumina	core	71%	
3% Rh/alumina	powder	7%	
0.5% Rh/alumina	core	7%	
0.5% Rh/alumina	powder	0.8%	

The data of TABLE II indicate that about ten times the percent of light hydrocarbons (i.e., C-10 or smaller) was formed over a catalyst-coated core relative to a powdered catalyst. The difference between the powder catalyst and coated core is believed to be due at least in part to the fact that the space velocity of gas through the powder reactor was 16 times the velocity through the core reactor.

Figure 4 is a system block diagram of a typical diesel engine system comprising diesel engine 12, fuel tank 16 and a primary fuel line 18 connecting fuel tank 16 to diesel engine 12 to provide diesel fuel A thereto. Typically, a fuel pump (not shown) is utilized to

facilitate the provision of diesel fuel A to engine 12 through fuel line 18. Engine 12 generates an exhaust gas stream that contains NO_x. Exhaust apparatus 20 defines a flow path for emissions of engine 12 from the engine into an exhaust manifold 28 and then into a conduit such as an exhaust pipe 30. The flow path continues through a conventional NO_x abatement catalyst 22, pipe 32 and a muffler 24, from which treated exhaust gases are discharged. The NO_x abatement catalyst may comprise, e.g., a honeycomb carrier coated with catalytic material effective at least for the reduction of NO_x. One suitable type of NO_x abatement catalyst is well-known in the art as a three-way catalyst (TWC catalyst). Such catalysts are known for their ability to substantially simultaneously catalyze the oxidation of hydrocarbons and carbon monoxide and the reduction of NO_x under generally stoichiometric conditions. Such catalysts are prepared by dispersing a platinum group metal, e.g., one or more platinum group metal compounds or complexes onto a relatively inert bulk support material. The ingredients and preparation procedure of such TWC catalysts is well-known in the art and is substantially described above in reference to platinum group metal-containing CPO catalyst materials, and so need not be repeated here.

In other embodiments, the NO_x abatement catalyst for use with the present invention may be specially formulated as a so-called lean NO_x catalyst. Such catalysts are known to comprise a catalyst and a NO_x sorbent. The NO_x sorbent stores NO_x during periods of lean (oxygen-rich) operation, and releases the stored NO_x during the rich (relatively fuel-rich) periods of operation. During periods of rich operation, the catalyst component of the catalyst/NO_x sorbent promotes the reduction of NO_x to nitrogen by reaction of NO_x (including NO_x released from the NO_x sorbent) with HC, CO and/or hydrogen present in the exhaust.

The use of NO_x storage (sorbent) components including alkaline earth metal oxides, such as oxides of Ca, Sr and Ba, alkali metal oxides such as oxides of K, Na, Li and Cs, and rare earth metal oxides such as oxides of Ce, La, Pr and Nd in combination with precious metal catalysts such as platinum dispersed on an alumina support, is known, as shown for example, at column 4, lines 19-25, of U.S. Patent 5,473,887 of S. Takeshima et al, issued on December 12, 1995 which is incorporated herein by reference, for background information. At column 4, lines 53-57, an exemplary composition is described as containing barium (an alkaline earth metal) and a platinum catalyst. The publication *Environmental Catalysts For A Better World And Life*, Proceedings of the 1st World Congress at Pisa, Italy, May 1-5, 1995, published by the Societa Chimica Italiana of Rome, Italy has, at pages 45-48 of the publication, an article entitled

"The New Concept 3-Way Catalyst For Automotive Lean-Burn Engine Storage and Reduction Catalyst", by Takahashi et al (below referred to as "the Takahashi et al paper"). This article discloses the preparation of catalysts of the type described in the above-mentioned Takeshima et al U.S. Patent 5,473,887 by impregnating precious metals, mainly platinum, and various
5 alkaline and alkaline earth metal oxides, mainly barium oxide, and rare earth oxides on refractory metal oxide supports, mainly alumina, and using these catalysts for NO_x purification of actual and simulated exhaust gases alternately under oxidizing (lean) and reducing (rich or stoichiometric) conditions. The conclusion is drawn in the last sentence on page 46, that NO_x was stored in the catalyst under oxidizing conditions and that the stored NO_x was then reduced
10 to nitrogen under stoichiometric and reducing conditions. Another suitable lean NO_x catalyst is described in U.S. Patent 5,451,558, "Process For the Reaction and Absorption of Gaseous Air Pollutants, Apparatus Therefor and Method of Making the Same", issued on September 19, 1995 to L. Campbell et al, which discloses a catalytic material for the reduction of NO_x in combustion exhaust, e.g., from a gas turbine in a power generating stack. The material
15 comprises an oxidation species and an adsorbent species. The oxidation species may comprise various metals including platinum group metals such as platinum, palladium or rhodium (see column 3, line 67, through column 4, line 3). The adsorbent species may comprise an alkali or alkaline earth metal carbonate, bicarbonate or hydroxide, and carbonates, especially sodium carbonate, potassium carbonate or calcium carbonate, are preferred. (See column 4, lines 24-
20 31.) The catalytic material is applied by coating the carrier with, e.g., platinum-coated alumina and then wetting the alumina with an alkali or alkaline earth metal carbonate solution, and then drying the wetted alumina (see column 5, line 9, through column 6, line 12). The use of a metal monolith support for the material is suggested at column 5, lines 48-58. Finally, U.S. Patent 5,874,057, "Lean NO_x Catalyst/Trap Method", issued on February 23, 1999 to M. Deeba et al,
25 discloses a method of NO_x abatement utilizing a composition comprising a NO_x abatement catalyst comprising platinum and, optionally, at least one other platinum group metal catalyst which is kept segregated from a NO_x sorbent material. The NO_x sorbent material may be one or more of oxides, carbonates, hydroxides and mixed oxides of one or more of various alkali metals including lithium, sodium and potassium, and alkaline earth metals including
30 magnesium, calcium, strontium and barium. As set forth at column 6, line 18 et seq of the '057 Patent, a platinum catalytic component is deemed to be essential and the utilization of the NO_x sorbent material in bulk form is taught as being advantageous. The '057 Patent also teaches the

optional use of ceria, for example, bulk ceria (ceria in fine particulate form), as a component of the composition. See column 3, lines 43-44. Any of the foregoing NO_x abatement catalysts and/or any others known in the art, may be used with the present invention.

In accordance with the present invention, exhaust apparatus 20 comprises an activated
5 reductant means 26. Secondary fuel line 18' connects fuel tank 16 to an inlet to activated reductant means 26 to provide a source of diesel fuel A thereto by means of pump 18a. Optionally, secondary fuel line 18' may branch off primary fuel line 18. Air inlet line 34 provides air or another source of oxygen to the activated reductant means 26 by means of an air pump 34a. The activated reductant means subjects a mixture of vapors of the diesel fuel with
10 the oxygen source and subjects the air-fuel mixture to activating conditions to produce activated diesel reductant and introduces the activated reductant into the conduit, i.e., into the exhaust gas stream, to provide reductant for the reduction of NO_x at NO_x abatement catalyst 22.

To make the operation of exhaust apparatus 20 responsive to changing conditions, exhaust apparatus 20 may also include a temperature sensor 52 mounted in exhaust pipe 30 at a
15 point suitable for the measurement of the temperature of exhaust gases entering NO_x abatement catalyst 22. There may be a control unit 54 that is responsive to sensor 52a and optionally to at least one other sensor (not shown) that detects NO_x in the gas stream and/or operating conditions under which NO_x is expected to be produced optionally including, e.g., sensing whether the exhaust gas is lean (i.e., $\lambda < 1$) (e.g., sensor 52b) or is being produced under lean
20 operating conditions. The control unit 54 is configured so that if sensors indicate that the exhaust gas entering NO_x abatement catalyst 22 is lean and is at a temperature below 200°C it may operate the supply of source hydrocarbons and the oxygen source (e.g., it may initiate pumps 18a and 34a) and also operate the activated reductant means. By providing activated diesel reductant at such temperatures, condensation of reductant on catalyst 22 as would occur
25 with unactivated diesel reductant is avoided and the activity and durability of NO_x abatement catalyst 22 is enhanced. When the lean exhaust gas temperature is 200°C or higher, the operation of the activated reductant means may optionally be stopped but the operation of the supply of source hydrocarbons and of the oxygen source may optionally continue because at such higher temperatures adequate NO_x conversion can be achieved with unactivated diesel
30 reductant. The exhaust gas treatment apparatus of the present invention treats NO_x over a broader temperature range than conventional NO_x abatement systems by providing activated reductant when the temperature of the exhaust gas is below about 200°C.

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Exhaust apparatus 20 may optionally comprise other abatement means (not shown), e.g., an oxidation catalyst, particulate trap, etc., that may be disposed in the flow path between the engine and muffler 24 to abate other pollutants in the exhaust gas, but preferably not between the activated reductant means at 26 and NO_x abatement catalyst 22.

5 A representative embodiment of an exhaust treatment apparatus as described above with regard to Figure 4 is seen in an exhaust treatment apparatus 20a, Figure 5A, in which the activated reductant means comprises a mixer that comprises a fuel injector 26a which is dimensioned and configured to receive diesel fuel and air via fuel line 18' and air inlet line 34, respectively, and to mix therein the air and fuel. As indicated above, a fuel pump may be
10 situated in line 18' to provide suitable pressure for injector 26a. If the vehicle is equipped with air brakes, air inlet line 34 may draw air therefrom. Otherwise, the vehicle may be equipped with an air pump 34a (Figure 4) specifically configured to provide air to injector 26a. Fuel injector 26a may be a conventional fuel injector that has been modified to accommodate an activating means comprising a glow plug 36 that extends into the discharge chamber. Glow
15 plug 36 may be a conventional electrically-heated glow plug and may serve to generate activating conditions in the mixer by heating the air-fuel mixture to a temperature at which the diesel fuel will undergo speciation, i.e., so that low molecular weight hydrocarbon species are produced, yielding activated diesel reductant that is more reactive for the reduction of NO_x than the diesel fuel entering injector 26a. The heating of glow plug 36 may be controlled by the
20 control unit 54 in response to input from the temperature sensor 52. When sensors associated with the engine or positioned in the exhaust gas stream indicate that the exhaust gas stream is lean and contains a significant quantity of NO_x, the control unit 54 may initiate one or both of fuel pump 18a and air pump 34a to provide a suitable amount of diesel fuel reductant to NO_x abatement catalyst 22. If the temperature of exhaust gas entering NO_x abatement catalyst 22 at
25 that time is below about 200°C, the control unit 54 may also initiate the heating of glow plug 36 so that the reductant introduced into the NO_x-containing gas stream comprises an activated reductant in accordance with the present invention. The activated diesel reductant vents from a discharge chamber in injector 26a and is thus introduced into the exhaust gas stream in pipe 30 to provide reductant for NO_x at NO_x abatement catalyst 22.

30 Figure 5B provides a schematic cross-sectional view of a portion of a particular embodiment of an apparatus generally similar to that of Figure 5A, the engine, fuel source, air source and the NO_x abatement catalyst being omitted to simplify the drawing. The exhaust gas

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treatment apparatus in Figure 5B comprises a mixer 126 that comprises a conventional fuel injector 126a mounted in a holder 50 which also defines a conduit 50c that provides fluid flow communication between the fuel injector outlet and the interior of the exhaust pipe 30. Holder 50 defines a fuel inlet 118 that communicates with the fuel inlet 126b of injector 126a and which is dimensioned and configured for connection to a supply of source hydrocarbon, e.g., to receive a fuel line such as fuel line 18' (Figure 5A). Holder 50 also defines an air inlet 134 that is dimensioned and configured for connection to a supply of oxygen, e.g., to receive an air inlet line such as line 34 (Figure 5A) so that the fuel dispersed by injector 126a via injector outlet 126c can be mixed with air or another source of oxygen in conduit 50c. Holder 50 is further configured to receive a heat source comprising a glow plug 36 that is positioned in conduit 50c to heat the air-fuel mixture to its speciation temperature before the mixture is introduced into exhaust pipe 30. A coupling portion 50a on holder 50 secures holder 50 to exhaust pipe 30 and provides a flow path via holder outlet 50b through which the heated air-fuel mixture is introduced as activated reductant into exhaust pipe 30. The activated reductant-exhaust gas mixture flows downstream to the NO_x abatement catalyst.

In an alternative embodiment of the present invention shown in Figure 6, exhaust treatment apparatus 20b comprises a mixer 26b that defines a mixing chamber therein and that accommodates an activating means comprising a miniature catalyst member 38 therein positioned to contact the fuel-oxygen mixture produced in mixer 26b. Mixer 26b may optionally comprise a modified fuel injector. Catalyst member 38 may be a plug-shaped member having a diameter of approximately 1 cm and a length of about 2.5 cm, and may be coated with a CPO catalytic material as described above. The catalyst member is positioned so that it can absorb sufficient heat from the exhaust gas in pipe 30 to attain a speciation temperature, even without a heat source, and so will facilitate speciation of the diesel fuel reductant into lower molecular weight hydrocarbon species prior to introducing the reductant into the exhaust gas stream. The embodiments of Figures 5A, 5B and Figure 6 provide mixing means for mixing oxygen and fuel and an activating means comprising either a heat source or a catalyst. In other embodiments, the activating means may optionally comprise both a heat source and a catalyst. For example, the heating element of glow plug 36 (Figure 5B) may be coated with a catalytic material effective to catalyze the partial oxidation (CPO) of the diesel fuel so that the glow plug heats both the CPO catalyst and the air-fuel mixture to a speciation temperature. The catalytic material, which may comprise, e.g., rhodium dispersed on alumina,

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may be coated onto the glow plug 36 in any conventional manner, but preferably, an anchor layer is deposited on the glow plug prior to application of the catalytic material. The anchor layer preferably comprises a nickel-aluminide material that is preferably thermally sprayed thereon in accordance with the teachings of U.S. patent application serial number 09/071,663, filed May 1, 1998, the disclosure of which is hereby incorporated herein by reference. Briefly restated, U.S. patent application 09/071,663 describes methods for applying anchor layers on various substrates. The disclosed methods, any of which may be employed to apply an anchor layer on the heating element of a glow plug, encompass thermal spraying processes in general, including plasma spraying, single wire plasma spraying, high velocity oxy-fuel spraying, combustion wire and/or powder spraying, electric arc spraying, etc. Electric arc spraying, e.g., twin wire arc spraying, of a metal (which term, as used herein and in the claims, includes mixtures of metals, including without limitation, metal alloys, pseudoalloys, and other intermetallic combinations) onto a metal or ceramic substrate was found to yield a structure having unexpectedly superior utility as a carrier for catalytic materials in the field of catalyst members. Twin wire arc spraying (encompassed herein by the term "wire arc spraying" and by the broader term "electric arc spraying") is a known process, as indicated by U.S. Patent 4,027,367 which is incorporated herein by reference. Briefly described, in the twin wire arc spray process, two feedstock wires act as two consumable electrodes. These wires are insulated from each other as they are fed to the spray nozzle of a spray gun in a fashion similar to wire flame guns. The wires meet in the center of a gas stream generated in the nozzle. An electric arc is initiated between the wires, and the current flowing through the wires causes their tips to melt. A compressed atomizing gas, usually air, is directed through the nozzle and across the arc zone, shearing off the molten droplets to form a spray that is propelled onto the substrate. Only metal wire feedstock can be used in an arc spray system because the feedstock must be conductive. The high particle temperatures created by the spray gun produce minute weld zones at the impact point on a metallic substrate. As a result, such electric arc spray coatings (sometimes referred to herein as "anchor layers") have good cohesive strength and a very good adhesive bond to the substrate.

The principal operating parameters in wire arc spraying include the voltage and amperage for the arc, the compression of the atomizing gas, the nozzle configuration and the stand-off from the substrate. The voltage is generally in the range of from 18 to 40 volts, and is typically in the range of from 28 to 32 volts; the current may be in the range of from about 100

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to 400 amps. The atomizing gas may be compressed to a pressure in the range of from about 30 to 70 psi. The nozzle configuration (e.g., slot aperture or cross aperture) and spray pattern vary in accordance with the desired nature of the anchor layer or may be chosen to accommodate the other parameters or the character of the substrate. A suitable stand-off is generally in the range of from about 4 to 10 inches from the substrate to the nozzle. Another operating parameter is the spray rate for the feedstock, a typical example of which would be 100 pounds per hour per 100 amps (4.5 kg/hr/100 amps). Still another parameter is the coverage or feedstock consumption rate, which may be, to give a particular example, 0.9 ounce per square foot per 0.001 inch thickness of the anchor layer. (It is typical to have a deposition efficiency of 70 percent (e.g., for spraying a plate) or less.)

Electric arc spray coatings are usually harder to finish (e.g., to grind down) and normally have higher spray rates than coatings of other thermal spray processes. Dissimilar electrode wires can be used to create an anchor layer containing a mixture of two or more different metal materials, referred to as a "pseudoalloy". Optionally, reactive gases can be used to atomize the molten feedstock to effect changes in the composition or properties of the applied anchor layer. On the other hand, it may be advantageous to employ an inert gas or at least a gas that does not contain oxygen or another oxidizing species. Oxygen, for example, may cause oxidation on the surface of a metal substrate or in the feedstock material and thus weaken the bond between the anchor layer and the substrate.

Anchor layers of a variety of compositions can be deposited on a substrate in accordance with the present invention by utilizing, without limitation, feedstocks of the following metals and metal mixtures: Ni, Ni/Al, Ni/Cr, Ni/Cr/Al/Y, Co/Cr, Co/Cr/Al/Y, Co/Ni/Cr/Al/Y, Fe/Al, Fe/Cr, Fe/Cr/Al, Fe/Cr/Al/Y, Fe/Ni/Al, Fe/Ni/Cr, 300 and 400 series stainless steels, and, optionally, mixtures of one or more thereof. One specific example of a metal useful for wire arc spraying onto a substrate in accordance with the present invention is a nickel/aluminum alloy that generally contains at least about 90% nickel and from about 3% to 10% aluminum, preferably from about 4% to 6% aluminum by weight. Such an alloy may contain minor proportions of other metals referred to herein as "impurities" totaling not more than about 2% of the alloy. A preferred specific feedstock alloy comprises about 95% nickel and 5% aluminum and may have a melting point of about 2642°F. Some such impurities may be included in the alloy for various purposes, e.g., as processing aids to facilitate the wire arc spraying process or the formation of the anchor layer, or to provide the anchor layer with favorable properties.

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It has also been found that electric arc spraying a metal onto a metal substrate yields an unexpectedly superior carrier for catalytic materials relative to carriers having metal anchor layers applied thereto by other methods. Catalytic materials have been seen to adhere better to a carrier comprising an electric arc sprayed anchor layers than to a carrier comprising a substrate without an intermediate layer applied thereto and even better than to a carrier comprising a substrate having a metal layer deposited thereon by plasma spraying. Absent an electric arc sprayed anchor layer, catalytic materials disposed on metal substrates, with or without intermediate layers between the substrate and the catalytic material, often did not adhere sufficiently well to the substrate to provide a commercially acceptable product. For example, a metal substrate having a metal intermediate layer that was plasma-sprayed thereon and having a catalytic material applied to the intermediate layer failed to retain the catalytic material, which flaked off upon routine handling, apparently due to a failure of the intermediate layer to bond with the substrate. The catalytic material on other carriers was seen to spall off upon normal use, apparently as a result of being subjected to a high gas flow rate, to thermal cycling, to the eroding contact of high temperature steam and other components of the exhaust gas stream, vibrations, etc. Electric arc spraying has therefore been found to improve the durability of catalyst members comprising catalytic materials carried on carrier substrates by improving their durability.

Surprisingly, it was found that electric arc spraying, of which wire arc spraying is a particular embodiment, of a metal onto a metal substrate results in a superior bond between the resulting anchor layer and the substrate relative to plasma spraying. An electric arc sprayed anchor layer is believed to have at least two characteristics that distinguish it from anchor layers applied by plasma spraying: a superior anchor layer-metallic substrate interface bond and a highly irregular or "rough" surface. It is believed that the anchor layer-metallic substrate interface bond may be the result of diffusion between the sprayed material and the metallic substrate that is achieved at their interface despite the relatively low temperature at which wire arc spraying is practiced. For example, the electric arc temperature may be not more than 10,000°F. In such case, the temperature of the molten feedstock is expected to be at a temperature of not more than about 5000°F, preferably in the range of 1000° to 4000° F, more preferably not more than about 2000°F. The low temperature is also believed to be responsible for the especially uneven surface of the anchor layer because the sprayed material cools on the substrate (whether metal or ceramic) to its freezing temperature so quickly that it does not flow

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significantly on the substrate surface and therefore does not smooth out. Instead, it freezes into an irregular surface configuration. Accordingly, the surface of the anchor layer has a rough profile that provides a superior physical anchor for catalytic components and materials disposed thereon. The rough profile appears to be the result of "pillaring", the formation of small, pillar-like structures resulting from the sequential deposition and freezing of one molten drop of feedstock material atop another.

It does not appear to be important to match the sprayed metal to the metal of the substrate, i.e., to the metal of the heating element of the glow plug. While the catalytic material and the optional anchor layer tend to insulate the glow plug and to interfere with heat transfer therefrom, a catalyzed glow plug does nevertheless provide a means for the catalytic partial oxidation of the diesel fuel.

The exhaust treatment apparatus 20c shown in Figure 7A comprises a mixing means comprising a conventional fuel injector 26c that receives air and fuel via lines 18' and 34 as described above and injects an unactivated mixture thereof into exhaust pipe 30. To facilitate activation, the fuel-air mixture is isolated from the exhaust gas within exhaust pipe 30 by a reductant conduit 40. The exhaust gases contacting conduit 40 may be sufficiently hot to create activating conditions within conduit 40 without an added heat source so that the reductant emitted at outlet 40a for mixture with the exhaust gas is activated for the reduction of NO_x at NO_x abatement catalyst 22. However, exhaust pipe 30 and conduit 40 may be adapted to accommodate a heat source structure that serves to create activating conditions therein. For example, Figure 7A shows a glow plug 36 for heating the air-fuel mixture and a CPO catalyst member 38a which are mounted in exhaust pipe 30 and conduit 40 for contact with the mixture. In addition, catalyst member 38a is surrounded by an electric heating element 42 comprising heating coils that serve to raise catalyst member 38a to its working (i.e., speciating) temperature. It will be understood that it is not necessary to use all the illustrated activating structures shown in Figure 7A, but rather that each may be used singly or they may be used in various combinations.

Another specific embodiment of the present invention is shown schematically in Figure 7B. In Figure 7B, activated reductant means 220 comprises a mixer comprising a fuel injector 126d that has a fuel inlet 126e, an air inlet 126f and an outlet 126g for emitting an air-fuel mixture produced therein. There is also a heating means comprising an electric heating element 142 connected to the injector outlet 126g. Heating element 142 defines an interior chamber

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within which a catalyst member 138 comprising a carrier core measuring 1 inch in length and 0.4 inch diameter that is coated with a CPO catalytic material. The catalyst member is mounted in heating element 142 with a gasket seal 138a. Heating element 142 has an outlet which is connected to and provides flow communication with exhaust pipe 30. In use, fuel and air are introduced into injector 126 and an air-fuel mixture is released therefrom into heating element 142. The air-fuel reductant mixture flows through catalyst member 138. The air-fuel mixture and the CPO catalyst are heated by heating element 142 to a temperature at which speciation occurs, to activate the reductant. The activated reductant flows through a heating unit outlet 142a into exhaust pipe 30 where it is mixed with the exhaust gases and from where it flows downstream to the NO_x abatement catalyst.

Although the present invention has been described in detail with respect to specific preferred embodiments thereof, it will be appreciated that various modifications thereto lie within the spirit and scope of the appended claims.

THE CLAIMS

What is claimed is:

- 5 1. An apparatus effective for generating activated reductant, comprising:
a mixer for receiving and mixing a source hydrocarbon and oxygen; and
activation means for speciating the source hydrocarbon to produce activated
reductant.
- 10 2. An apparatus for generating activated hydrocarbon species from source
hydrocarbons, comprising:
a mixer having inlets for receiving the source hydrocarbon and oxygen, a mixing
chamber for creating a mixture of the source hydrocarbon and oxygen and an outlet for
discharging activated hydrocarbon species; and
15 a catalyst disposed for contact with the mixture, the catalyst being effective for
activating the source hydrocarbon.
3. The apparatus of claim 2 wherein the catalyst is disposed in the mixer.
- 20 4. The apparatus of claim 3 comprising a glow plug comprising a catalyzed heating
element disposed in the mixer.
5. An apparatus for generating activated hydrocarbon species from source
hydrocarbons, comprising:
25 a mixer having inlets for receiving the source hydrocarbon and oxygen, a mixing
chamber for creating a mixture of the source hydrocarbon and oxygen and an outlet for
discharging activated hydrocarbon species; and
a heating element positioned to generate activated hydrocarbons from the mixture of
the source hydrocarbon and oxygen.
- 30 6. The apparatus of claim 5 wherein the heating element is disposed in the mixer.

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7. The apparatus of claim 6 comprising a glow plug mounted thereon with the heating element in the mixer.

8. The apparatus of claim 5 wherein the heating element is positioned to contact the mixture discharged from the outlet of the mixer to generate activated hydrocarbon species therefrom.

9. The apparatus of claim 8 wherein the heating element has a heater inlet connected to the mixer outlet for receiving the mixture of source hydrocarbon and oxygen and a heater outlet for discharging activated hydrocarbon species.

10. The apparatus of claim 9 further comprising a catalyst in the heating element positioned to contact the mixture prior to discharge of the activated hydrocarbon species from the heater outlet.

15

11. The apparatus of any one of claims 1 through 10 further comprising a temperature sensor for sensing the temperature of a gas stream and at least one oxygen sensor for sensing whether such gas stream is lean, and further comprising a control unit responsive to the sensors, for initiating the apparatus when the oxygen sensor indicates a lean gas stream and the temperature sensor indicates a temperature of less than 200°C.

20

12. The apparatus of claim 11 wherein the control unit is configured to initiate the apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C.

25

13. The apparatus of claim 1 or claim 2 further comprising an air pump connected for delivering oxygen to the mixer and a fuel pump connected for delivering source hydrocarbon to the mixer.

30

14. The apparatus of claim 13 further comprising a temperature sensor for sensing the temperature of a gas stream and an oxygen sensor for sensing whether the gas stream is lean, and further comprising a control unit responsive to the sensors, for initiating the apparatus when

the oxygen sensor indicates a lean gas stream and the temperature sensor indicates a temperature of less than 200°C, wherein activating the apparatus comprises activating the air pump and the fuel pump.

5 15. The apparatus of claim 14 wherein the control unit is configured to initiate the apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C.

10 16. The apparatus of any one of claims 2 through 10 further comprising an air pump connected to a mixer inlet for delivering oxygen to the mixer and a fuel pump connected to a mixer inlet for delivering source hydrocarbon to the mixer.

15 17. The apparatus of claim 16 further comprising a temperature sensor for sensing the temperature of a gas stream and an oxygen sensor for sensing whether the gas stream is lean, and further comprising a control unit responsive to the sensors, for initiating the apparatus when the oxygen sensor indicates a lean gas stream and the temperature sensor indicates a temperature of less than 200°C, wherein activating the apparatus comprises activating the air pump and the fuel pump.

20 18. The apparatus of claim 17 wherein the control unit is configured to initiate the apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C.

25 19. An apparatus effective at least for the reduction of oxides of nitrogen (NO_x) in a gas stream, the apparatus comprising:

 a supply of source hydrocarbon;

 a source of oxygen;

 a mixer for receiving source hydrocarbon from the supply and for receiving the oxygen and for producing a mixture thereof;

30 activation means for speciating the source hydrocarbon in the mixture to produce activated reductant and providing the activated reductant to the gas stream; and

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a NO_x-reduction catalyst positioned for contact with the gas stream with the activated reductant therein.

20. The apparatus of claim 19 wherein the activation means comprises a glow plug
5 comprising a catalyzed heating element disposed in the mixing chamber.

21. An apparatus effective at least for the reduction of oxides of nitrogen (NO_x) in a gas stream, the apparatus comprising:

a supply of source hydrocarbon;

10 a source of oxygen;

a mixer having inlets for receiving the source hydrocarbon and oxygen, a mixing chamber for creating a mixture of the source hydrocarbon and oxygen and an outlet for discharging activated hydrocarbon species to the gas stream;

a catalyst in the mixing chamber effective for activating the source hydrocarbon;

15 and

a NO_x-reduction catalyst positioned for contact with the gas stream and the activated reductant therein.

22. The apparatus of claim 21 wherein the source hydrocarbon comprises diesel fuel.
20

23. An apparatus effective at least for the reduction of oxides of nitrogen (NO_x) in a gas stream, the apparatus comprising:

a mixer having inlets for receiving the source hydrocarbon and oxygen, a mixing chamber for creating a mixture of the source hydrocarbon and oxygen and having an outlet for
25 discharging activated hydrocarbon species to the gas stream; and

a heating element positioned to generate activated hydrocarbons from the mixture of the source hydrocarbon and oxygen; and

a NO_x-reduction catalyst positioned for contact with the gas stream and the activated reductant therein.

30

24. The apparatus of claim 23 wherein the heating element is disposed in the mixer.

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25. The apparatus of claim 24 comprising a glow plug mounted thereon with the heating element in the mixer.

26. The apparatus of claim 24 wherein the heating element is positioned to contact the mixture discharged from the outlet of the mixer to generate activated hydrocarbon species therefrom.

27. The apparatus of claim 26 wherein the heating element has a heater inlet connected to the mixer outlet for receiving the mixture of source hydrocarbon and oxygen and a heater outlet for discharging activated hydrocarbon species.

28. The apparatus of claim 27 comprising a catalyst in the heating element positioned to contact the mixture prior to discharge of the activated hydrocarbon species from the heater outlet.

15

29. The apparatus of any one of claims 19-28 further comprising a temperature sensor for sensing the temperature of a gas stream and an oxygen sensor for sensing whether such gas stream is lean, and further comprising a control unit responsive to the sensors, for initiating the apparatus when the oxygen sensor indicates a lean gas stream and the temperature sensor indicates a temperature of less than 200°C.

20

30. The apparatus of claim 29 wherein the control unit is configured to initiate the apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C.

25

31. The apparatus of claim 19 further comprising an air pump connected for delivering oxygen to the mixer and a fuel pump connected for delivering source hydrocarbon to the mixer.

32. The apparatus of claim 31 further comprising a temperature sensor for sensing the temperature of the gas stream contacting the NO_x-reduction catalyst and an oxygen sensor for sensing whether the gas stream is lean, and further comprising a control unit responsive to the sensors, for initiating the apparatus when the oxygen sensor indicates a lean gas stream and the

30

-32-

temperature sensor indicates a temperature of less than 200°C, wherein activating the apparatus comprises activating the air pump and the fuel pump.

33. The apparatus of claim 32 wherein the control unit is configured to initiate the apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C.

34. The apparatus of any of claims 19 through 28 further comprising an air pump connected to a mixer inlet for delivering oxygen to the mixer and a fuel pump connected to a mixer inlet for delivering source hydrocarbon to the mixer.

35. The apparatus of claim 34 further comprising a temperature sensor for sensing the temperature of the gas stream contacting the NO_x-reduction catalyst and an oxygen sensor for sensing whether the gas stream is lean, and further comprising a control unit responsive to the sensors, for initiating the apparatus when the oxygen sensor indicates a lean gas stream and the temperature sensor indicates a temperature of less than 200°C, wherein activating the apparatus comprises activating the air pump and the fuel pump.

36. The apparatus of claim 35 wherein the control unit is configured to initiate the apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C.

37. A method for producing an activated hydrocarbon species, comprising mixing a source hydrocarbon with oxygen and subjecting the mixture to activating conditions.

38. The method of claim 37 wherein the source hydrocarbon comprises diesel fuel.

39. The method of claim 37 or claim 38 comprising contacting the mixture with a catalytic material effective to facilitate speciation of the source hydrocarbon.

40. The method of claim 37 or claim 38 comprising heating the mixture to a temperature of at least about 350°C.

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41. The method of claim 39 comprising contacting the mixture at a temperature lower than 350°C with a catalyst effective to facilitate speciation at such lower temperature.

42. The method of claim 41 comprising contacting the mixture with the catalyst at a
5 temperature in the range of from about 200°C to 340°C.

43. An activated hydrocarbon reductant produced by a method comprising mixing a source hydrocarbon with oxygen and subjecting the mixture to activating conditions.

10 44. The activated hydrocarbon species produced by the method of claim 37 wherein the source hydrocarbon comprises diesel fuel.

45. The activated hydrocarbon species produced by the method of claim 37 or claim 38 wherein the method further comprises contacting the mixture with a catalytic material effective
15 to facilitate speciation of the source hydrocarbon.

46. The activated hydrocarbon species produced by the method of claim 37 or claim 38 further comprising heating the mixture to a temperature of at least about 350°C.

20 47. The activated hydrocarbon species produced by the method of claim 39 and further comprising contacting the mixture at a temperature lower than 350°C with a catalyst effective to facilitate speciation at such lower temperature.

48. The activated hydrocarbon species produced by the method of claim 42 and further
25 comprising contacting the mixture with the catalyst at a temperature in the range of from about 200°C to 340°C.

49. A method for reducing oxides of nitrogen (NO_x) in a lean gas stream, comprising:
creating a fuel-oxygen mixture by mixing diesel fuel vapor with oxygen, subjecting
30 the fuel-oxygen mixture to activating conditions to create an activated diesel reductant;
mixing the activated diesel reductant into the gas stream; and

-34-

contacting the gas stream with the activated diesel reductant therein with a NO_x-reduction catalyst.

50. The method of claim 49 comprising heating the fuel-oxygen mixture to about 350°C
5 before adding the fuel-oxygen mixture to the gas stream.

51. The method of claim 49 comprising contacting the fuel-oxygen mixture with a catalytic material.

10 52. The method of claim 49, claim 50 or claim 51 comprising mixing the activated diesel reductant with the gas stream at a temperature below 200°C.

53. The method of claim 52 comprising mixing the activated diesel reductant with the gas stream at a temperature in the range of about 140°C to 200°C.
15

54. The method of claim 53 comprising mixing the activated diesel reductant with the gas stream at a temperature in the range of about 140°C to 160°C.

55. A method of operating an apparatus for the reduction of NO_x in a lean gas stream,
20 comprising:
 flowing the gas stream into contact with a NO_x-reduction catalyst;
 sensing the temperature of the gas stream contacting the NO_x-reduction catalyst; and
 introducing activated diesel reductant into the gas stream for contact with the NO_x-
reduction catalyst when the temperature of the gas stream is in the range of 140°C to 200°C.
25

56. The method of claim 55 comprising introducing the activated diesel reductant into the gas stream when the temperature of the gas stream is in the range of 140°C to 160°C.

57. A method for operating an apparatus effective at least for the reduction of oxides of
30 nitrogen (NO_x) in a gas stream, the apparatus comprising a supply of source hydrocarbon, a source of oxygen, activated reductant means for mixing the source hydrocarbon and oxygen, speciating the source hydrocarbon to produce activated reductant and providing the activated

-35-

reductant to the gas stream, and a NO_x-reduction catalyst positioned for contact with the gas stream with the activated reductant therein, the method comprising operating the activated reductant means, the supply of source hydrocarbon, and the source of oxygen when the gas stream is lean and when the temperature of the gas stream contacting the NO_x-reduction catalyst is at a temperature less than 200°C.

58. The method of claim 57 comprising operating the activated reductant means when the temperature of the exhaust gas is in the range of about 140°C to 160°C.

59. In a glow plug comprising a heating element extending from a plug body, the improvement comprising that a coating of catalytic material is carried on the heating element, the catalytic material being effective to facilitate the speciation of a source hydrocarbon.

60. The glow plug of claim 59 wherein the improvement further comprises an anchor layer on the heating element between the heating element and the catalytic material.

61. The glow plug of claim 60 wherein the improvement further comprises that the anchor layer comprises a metal that is thermally sprayed onto the heating element of the glow plug.

62. The glow plug of claim 61 wherein the improvement further comprises that the anchor layer is electric arc sprayed onto the heating element of the glow plug.

63. The glow plug of claim 61 wherein the improvement further comprises that the anchor layer is deposited by electric arc spraying a metal feedstock selected from the group consisting of nickel, Ni/Al, Ni/Cr, Ni/Cr/Al/Y, Co/Cr, Co/Cr/Al/Y, Co/Ni/Cr/Al/Y, Fe/Al, Fe/Cr, Fe/Cr/Al, Fe/Cr/Al/Y, Fe/Ni/Al, Fe/Ni/Cr, 300 series stainless steels, 400 series stainless steels, and mixtures of two or more thereof.

64. The glow plug of claim 63 wherein the improvement further comprises that the anchor layer comprises nickel and aluminum.

-36-

65. The glow plug of claim 64 wherein the improvement comprises that the aluminum comprises from about 3 to 10 percent of the combined weights of nickel and aluminum in the anchor layer.

5 66. The glow plug of claim 64 wherein the improvement comprises that the aluminum comprises from about 4 to 6 percent of the combined weights of nickel and aluminum in the anchor layer.

10 67. The glow plug of claim 59 wherein the improvement comprises that the catalytic material is deposited on the anchor layer and comprises a refractory metal oxide support on which one or more catalytic metal components are dispersed.

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SH 1078

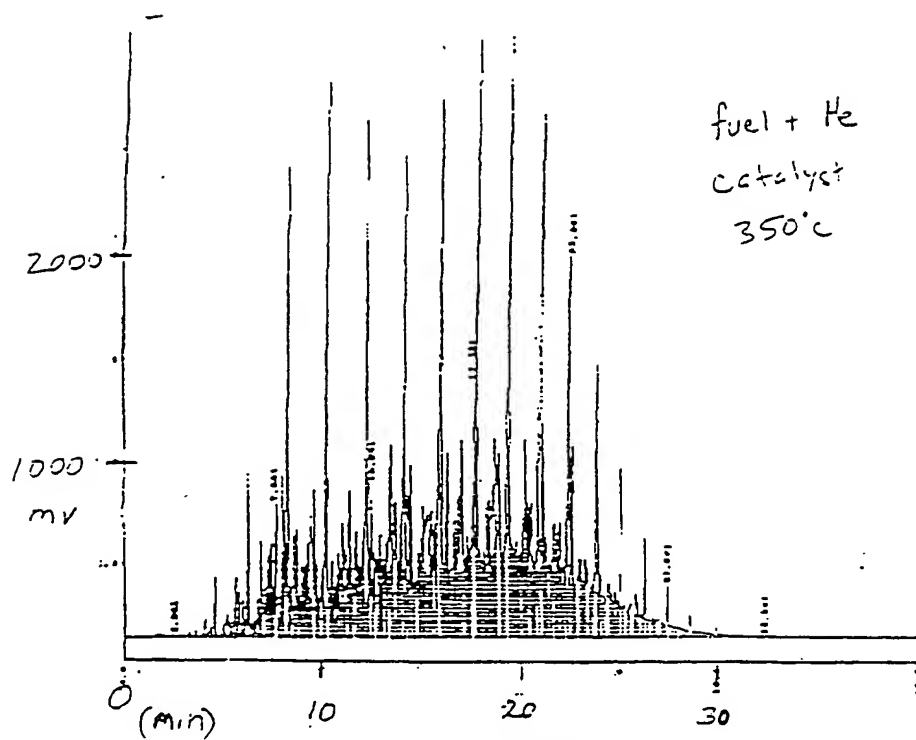


FIG. 1A

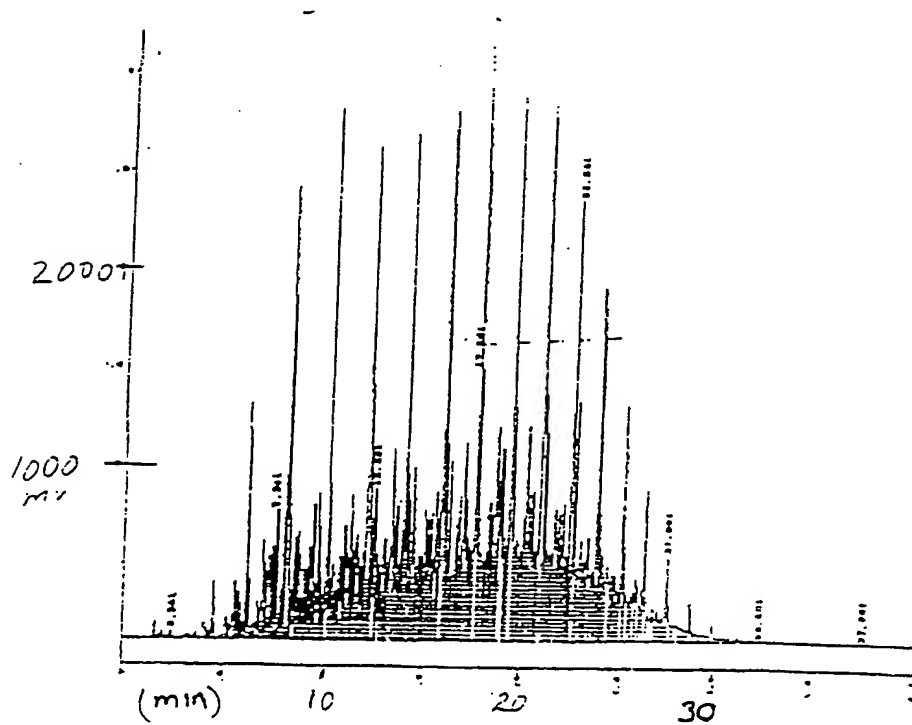


FIG. 1B

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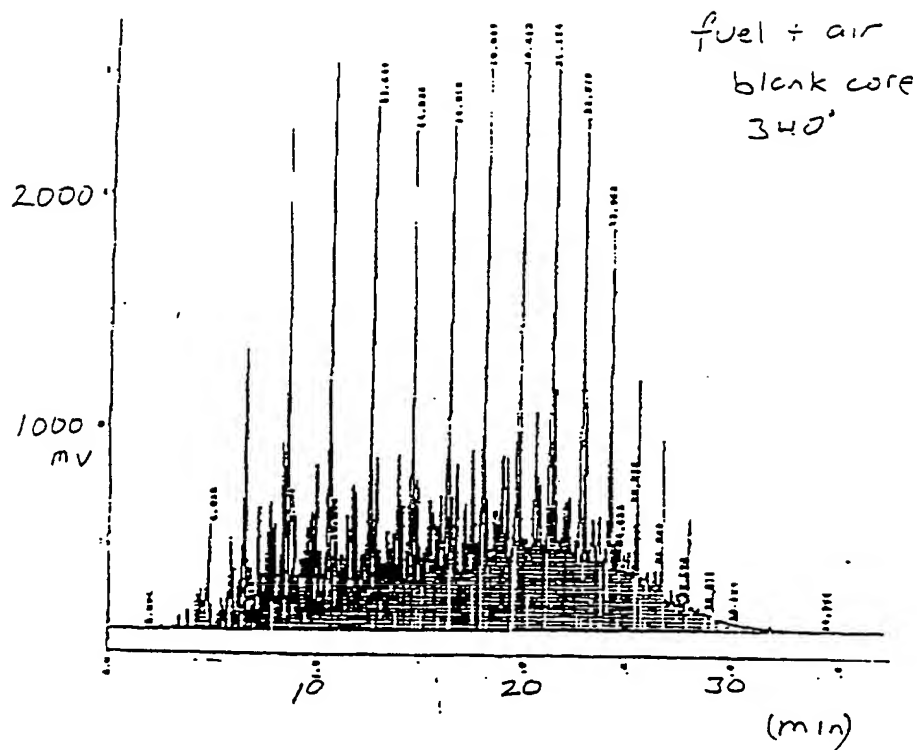


FIG.1C

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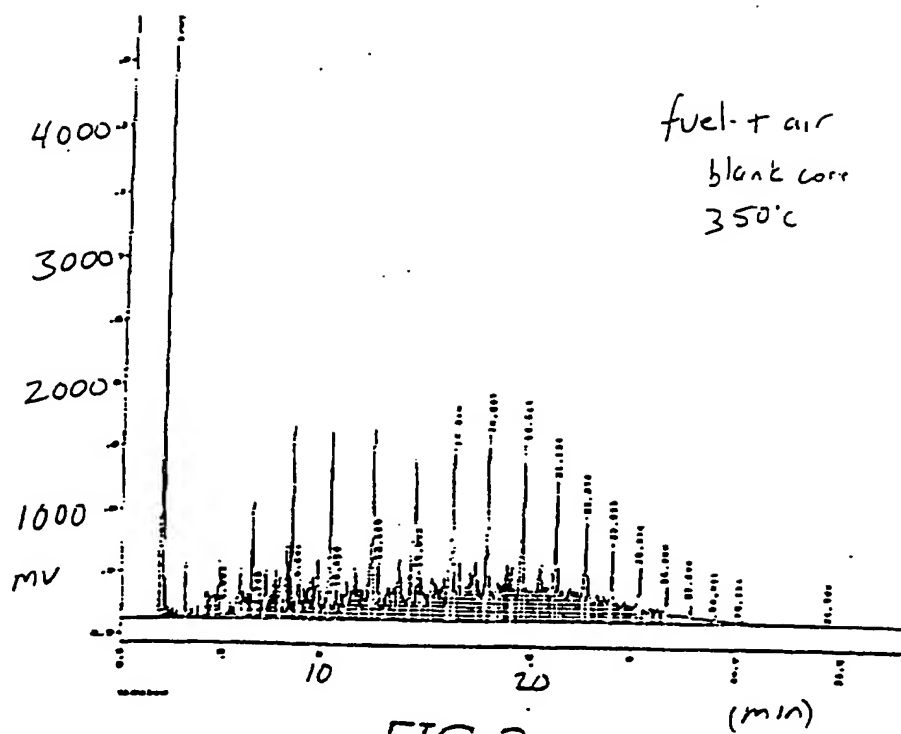


FIG. 2

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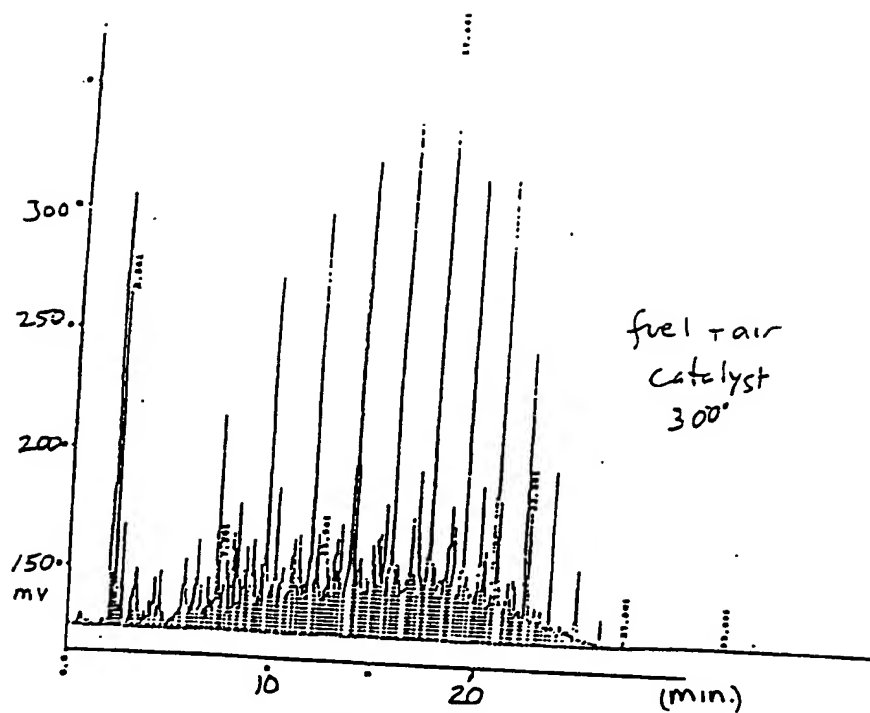


FIG. 3A

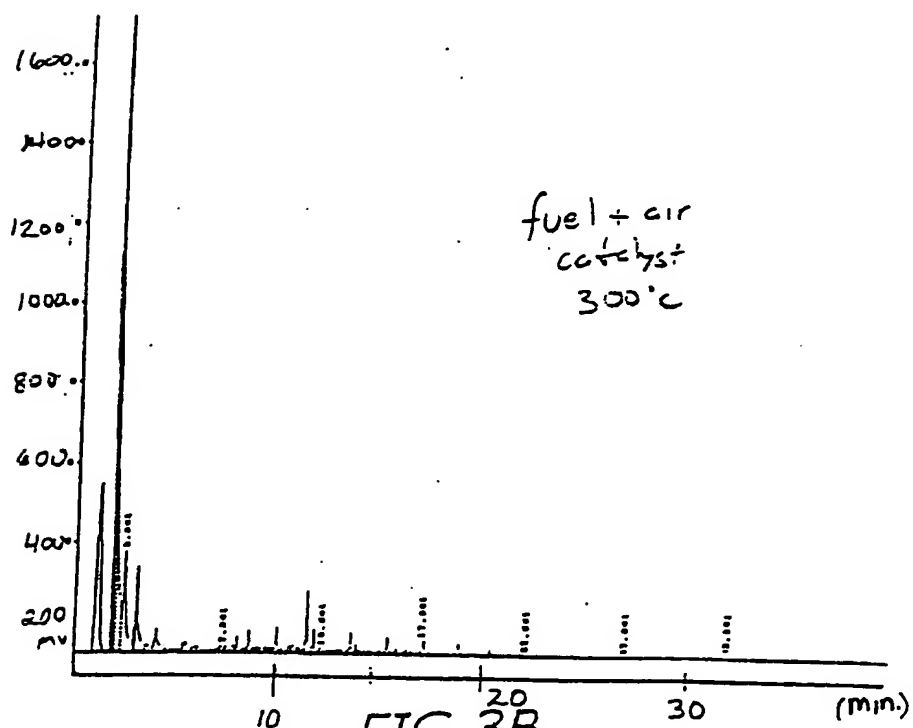


FIG. 3B

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SH 5 of 8

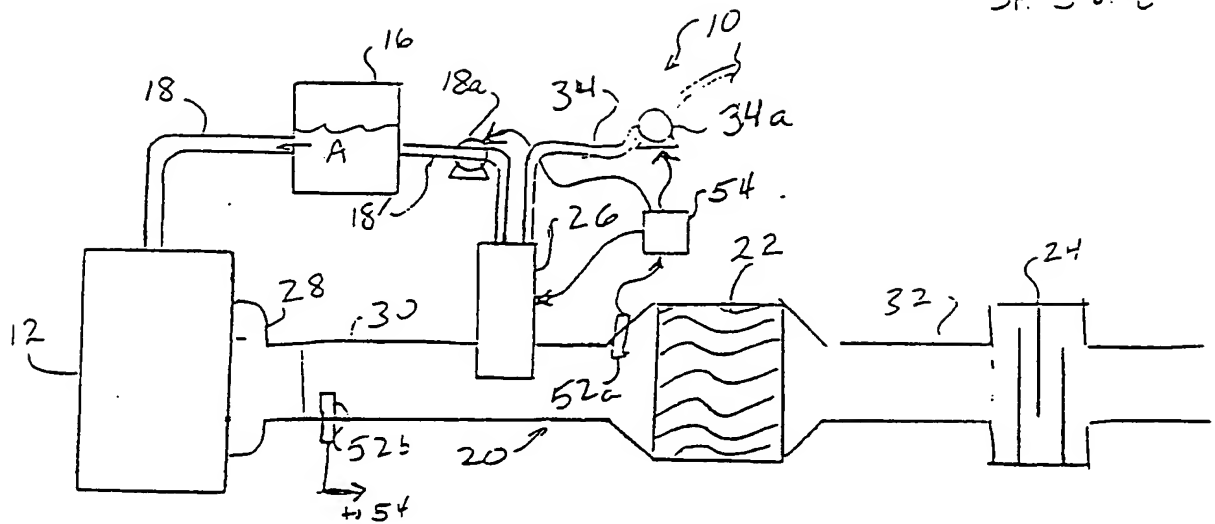
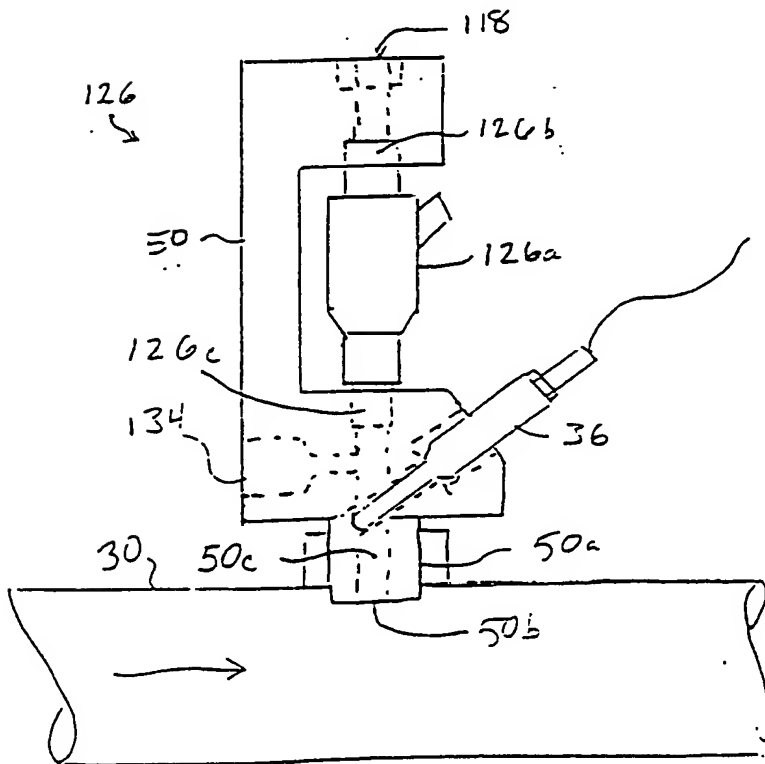
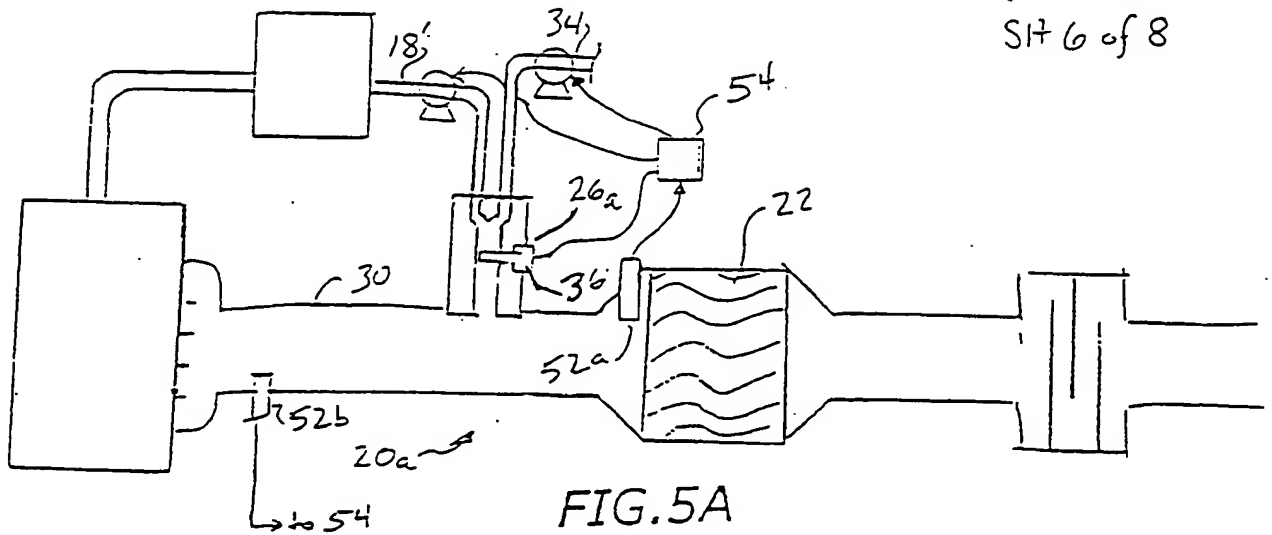


FIG. 4

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Sheet 6 of 8



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SH 7 of 8

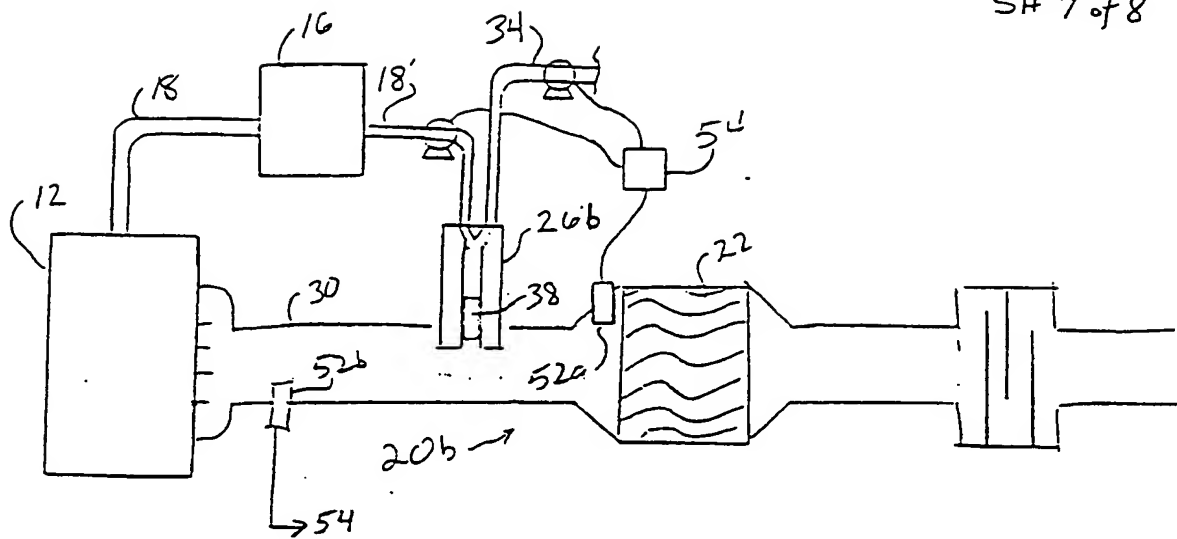


FIG. 6

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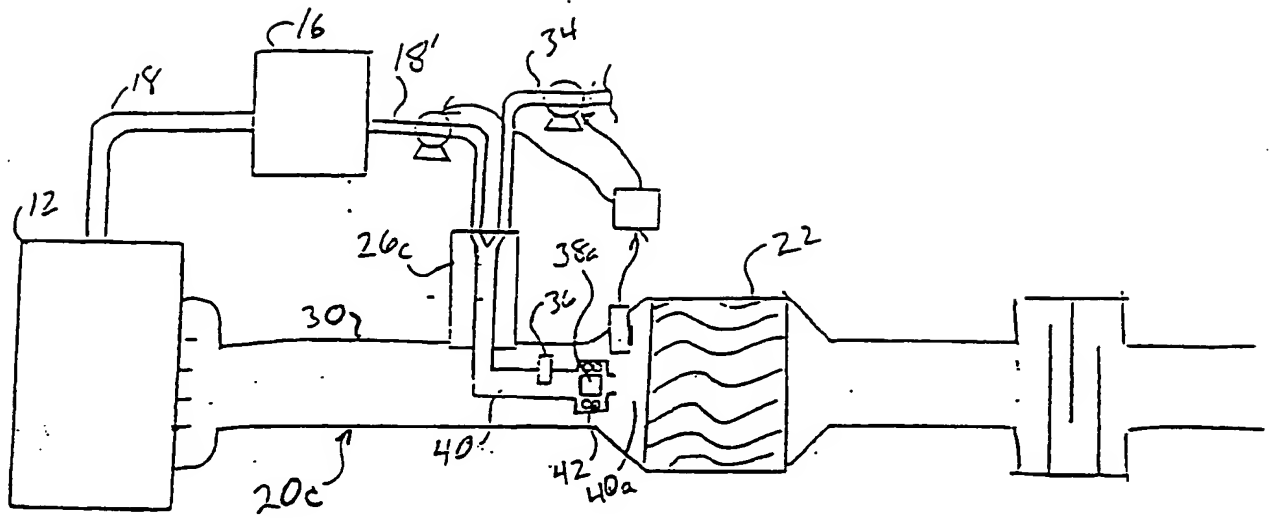


FIG. 7A

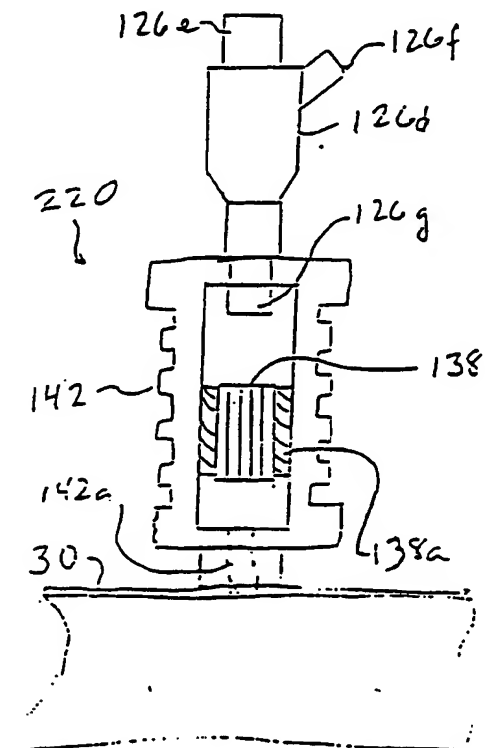


FIG. 7B

INTERNATIONAL SEARCH REPORT

Int l Application No
PCT/US 00/30507

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 F01N3/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 586 433 A (WEISWEILER WERNER ET AL) 24 December 1996 (1996-12-24)	1-3, 5, 13, 16, 19, 21-23, 31, 34, 37-51
A	the whole document	24, 55, 57
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 579 (M-1698), 7 November 1994 (1994-11-07) -& JP 06 212952 A (MITSUBISHI MOTORS CORP), 2 August 1994 (1994-08-02)	1-3, 13, 16, 19, 21, 22, 31, 34, 37-39, 41, 43-45, 49, 51
A	abstract; figure 1	55, 57

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

2 March 2001

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Int ional Application No
PCT/US 00/30507

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A	column 7, line 19 - line 52; figure 6	5,23,49, 51,55,57
X	GB 2 308 820 A (KOMATSU MFG CO LTD) 9 July 1997 (1997-07-09)	1,5,6, 19,23, 24,37, 38,40, 43,44, 46,49
A	abstract page 5, last paragraph -page 7, paragraph 2 page 11, paragraph 2 -page 12, paragraph 1 page 16, last paragraph -page 17, paragraph 1	2,21,22, 55,57
X,P	EP 0 971 102 A (MITSUBISHI MOTORS CORP) 12 January 2000 (2000-01-12)	1,5,8,9, 13,16, 37,38, 40,43, 44,46, 49,50
A	abstract column 4, line 22 -column 7, line 45; figure 1	2,11,14, 17,19, 21-23, 26,27, 29,31, 32,34, 35,55,57
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INTERNATIONAL SEARCH REPORT

Int. l. Application No

PCT/US 00/30507

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN vol. 018, no. 389 (M-1642), 21 July 1994 (1994-07-21) -& JP 06 108825 A (MITSUBISHI MOTORS CORP), 19 April 1994 (1994-04-19) cited in the application</p> <p>abstract; figure 1 -& DATABASE WPI Section Ch, Week 199420 Derwent Publications Ltd., London, GB; Class E36, AN 1994-164561 XP002161899 abstract</p>	<p>1,2,5, 19, 21-23, 37-39, 43-45, 49,51, 55,57</p>
A	<p>EP 0 499 931 A (VOLKSWAGENWERK AG ;BAYER AG (DE)) 26 August 1992 (1992-08-26) cited in the application abstract page 2, line 29 - line 30</p>	<p>2,21,39, 45,51,59</p>
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Information on patent family members

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6 November 2000 (06.11.2000)

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09/437,991 10 November 1999 (10.11.1999) US

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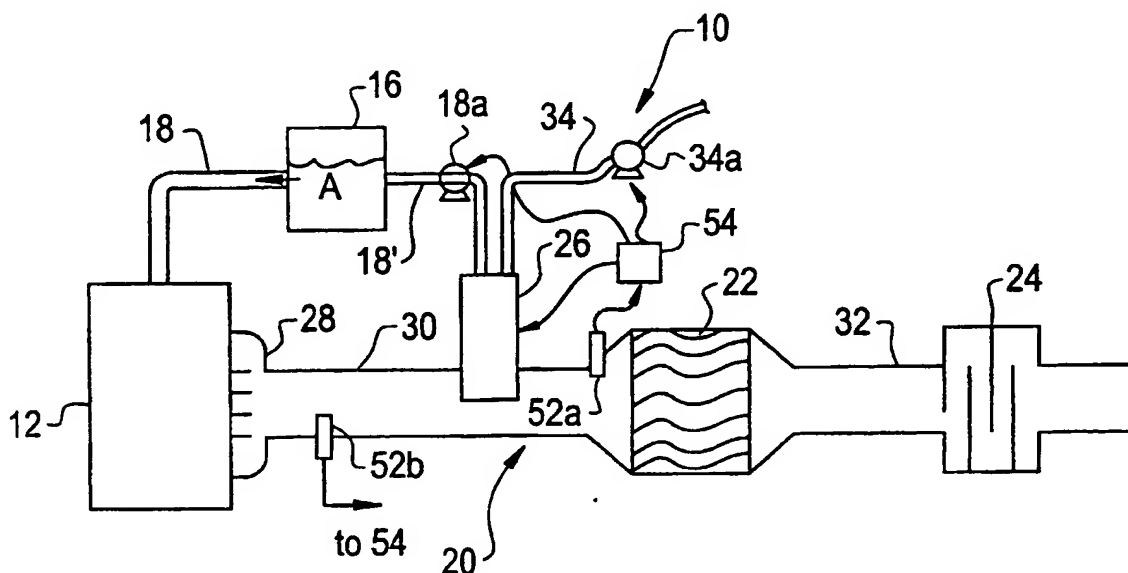
(81) Designated States (*national*): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— with international search report
— with amended claims

[Continued on next page]

(54) Title: METHOD AND APPARATUS TO PROVIDE REDUCTANT FOR NO_x



(57) Abstract: A method and apparatus for providing a reductant to a NO_x abatement means for a diesel engine, in which the diesel fuel is used as the reductant. The diesel fuel (A) is mixed with oxygen and is "activated", i.e., a significant portion of the diesel fuel is converted into lightweight hydrocarbon species, before being used as reductant for the NO_x. A catalytic partial oxidation (CPO) catalyst (e.g., 38) and/or a heating element (e.g., 42 or 142) can facilitate activation of the oxygen and fuel mixture. The CPO catalyst may be incorporated into injection means (26b) for the reductant. In one embodiment, a catalyzed glow plug is used to activate the reductant. Methods and apparatuses for reducing NO_x are also disclosed.

WO 01/34950 A1



Date of publication of the amended claims:

27 September 2001

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

AMENDED CLAIMS

[received by the International Bureau on 11 May 2001 (11.05.01);
original claims 1-67 replaced by new claims 1-73 (8 pages)]

- 5 1. Canceled.
2. Canceled.
3. Canceled.
- 10 4. Canceled.
5. An apparatus for generating activated reductant from source hydrocarbons without the use of a catalyst member, the apparatus consisting essentially of:
- 15 a mixer having inlets for receiving the source hydrocarbon and oxygen, a mixing chamber for creating a mixture of the source hydrocarbon and oxygen and an outlet for discharging activated hydrocarbon species; and
- a heating element capable of heating the mixture to at least about 350°C to generate activated hydrocarbons therefrom.
- 20 6. The apparatus of claim 5 wherein the heating element is disposed in the mixer.
7. The apparatus of claim 6 comprising a glow plug mounted thereon with the heating element in the mixer.
- 25 8. The apparatus of claim 5 wherein the heating element is positioned to contact the mixture discharged from the outlet of the mixer to generate activated hydrocarbon species therefrom.
- 30 9. The apparatus of claim 8 wherein the heating element has a heater inlet connected to the mixer outlet for receiving the mixture of source hydrocarbon and oxygen and a heater outlet for discharging activated hydrocarbon species.

10. Canceled.

11. The apparatus of any one of claims 5 through 9 further comprising a temperature sensor for sensing the temperature of a gas stream and at least one oxygen sensor for sensing whether such gas stream is lean, and further comprising a control unit responsive to the sensors, the control unit operating the apparatus when the oxygen sensor indicates a lean gas stream and the temperature sensor indicates a temperature of less than about 200°C.

12. The apparatus of claim 11 wherein the control unit is configured to operate the apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C.

13. Canceled.

14. Canceled.

15. Canceled.

16. The apparatus of any one of claims 5 through 9 further comprising an air pump connected to a mixer inlet for delivering oxygen to the mixer and a fuel pump connected to a mixer inlet for delivering source hydrocarbon to the mixer.

17. The apparatus of claim 16 further comprising a temperature sensor for sensing the temperature of a gas stream and an oxygen sensor for sensing whether the gas stream is lean, and further comprising a control unit responsive to the sensors, the control unit operating the apparatus when the oxygen sensor indicates a lean gas stream and the temperature sensor indicates a temperature of less than 200°C, wherein operating the apparatus comprises operating the air pump and the fuel pump.

18. The apparatus of claim 17 wherein the control unit is configured to operate the apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C.

19. Canceled.

20. Canceled.

21. An apparatus effective at least for the reduction of oxides of nitrogen (NO_x) in a gas stream, the apparatus comprising:

5 a supply of source hydrocarbon;

a source of oxygen;

a mixer having inlets for receiving the source hydrocarbon and oxygen, a mixing chamber for creating a mixture of the source hydrocarbon and oxygen in amounts that provide a $\text{O}_2\text{:C}$ ratio in the range of from about 0.3:1 to 0.8:1 and having an outlet to the gas stream;

10 a catalyst comprising a platinum group metal effective for the catalytic partial oxidation of the source hydrocarbon to produce activated reductant therefrom; and

a NO_x -reduction catalyst positioned for contact with the gas stream and the activated reductant therein.

15 22. Canceled.

23. An apparatus effective at least for the reduction of oxides of nitrogen (NO_x) in a gas stream, the apparatus comprising:

20 a mixer having inlets for receiving the source hydrocarbon and oxygen, a mixing chamber for creating a mixture of the source hydrocarbon and oxygen and having an outlet for discharging activated hydrocarbon species to the gas stream; and

a non-catalyzed heating element positioned to generate activated hydrocarbons from the mixture of the source hydrocarbon and oxygen; and

25 a NO_x -reduction catalyst positioned for contact with the gas stream and the activated reductant therein.

24. The apparatus of claim 23 wherein the heating element is disposed in the mixer.

30 25. The apparatus of claim 24 comprising a glow plug mounted thereon with the heating element in the mixer.

26. The apparatus of claim 24 wherein the heating element is positioned to contact the mixture discharged from the outlet of the mixer to generate activated hydrocarbon species therefrom.

5 27. The apparatus of claim 26 wherein the heating element has a heater inlet connected to the mixer outlet for receiving the mixture of source hydrocarbon and oxygen and a heater outlet for discharging activated hydrocarbon species.

28. Canceled.

10 29. The apparatus of any one of claims 21 or 23 through 27 further comprising a temperature sensor for sensing the temperature of a gas stream and an oxygen sensor for sensing whether such gas stream is lean, and further comprising a control unit responsive to the sensors, for operating the apparatus when the oxygen sensor indicates a lean gas stream and the
15 temperature sensor indicates a temperature of less than about 200°C.

30. The apparatus of claim 29 wherein the control unit is configured to operate the apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C.

20 31. Canceled.

32. Canceled.

25 33. Canceled.

34. The apparatus of any of claims 21 or 23 through 27 further comprising an air pump connected to a mixer inlet for delivering oxygen to the mixer and a fuel pump connected to a mixer inlet for delivering source hydrocarbon to the mixer.

30 35. The apparatus of claim 34 further comprising a temperature sensor for sensing the temperature of the gas stream contacting the NO_x-reduction catalyst and an oxygen sensor for sensing whether the gas stream is lean, and further comprising a control unit responsive to the sensors, for operating the apparatus when the oxygen sensor indicates a lean gas stream and the

temperature sensor indicates a temperature of less than 200°C, wherein operating the apparatus comprises operating the air pump and the fuel pump.

36. The apparatus of claim 35 wherein the control unit is configured to operate the
5 apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C.

37. Canceled.

10 38. Canceled.

39. Canceled.

15 40. Canceled.

41. Canceled.

42. Canceled.

20 43. An activated hydrocarbon reductant produced by a method comprising mixing a source hydrocarbon with oxygen in quantities which provide a O₂:C ratio in the range of from about 0.3:1 to 0.8:1, and heating the mixture to a temperature of at least about 350°C in the absence of a catalyst.

25 44. The activated hydrocarbon species produced by the method of claim 43 wherein the source hydrocarbon comprises diesel fuel.

45. Canceled.

30 46. Canceled.

47. Canceled.

48. Canceled.

49. A method for reducing oxides of nitrogen (NO_x) in a lean gas stream, comprising:
adding activated reductant to the gas stream when the gas stream is at a temperature
below about 200°C ; and
contacting the gas stream with the activated reductant therein with a NO_x -reduction
5 catalyst.

50. The method of claim 49 comprising generating the activated reductant by mixing a
source hydrocarbon with oxygen and in proportions that provide a $\text{O}_2:\text{C}$ ratio in the range of
from about 0.3 to 0.8:1 and heating the mixture to about 350°C to produce the activated
10 reductant without the use of a catalyst.

51. The method of claim 49 comprising generating the activated reductant by mixing a
source hydrocarbon with oxygen and in proportions that provide a $\text{O}_2:\text{C}$ ratio in the range of
from about 0.3 to 0.8:1 and contacting the mixture with a catalyst comprising a platinum group
15 metal effective to catalyze the catalytic partial oxidation of the source hydrocarbon to produce
the activated reductant.

52. Canceled.

20 53. The method of claim 49, 50 or 51 comprising mixing the activated reductant with
the gas stream at a temperature in the range of from about 140°C to 200°C .

54. The method of claim 53 comprising mixing the activated diesel reductant with the
gas stream at a temperature in the range of about 140°C to 160°C .

25

55. Canceled.

56. Canceled.

30 57. Canceled.

58. Canceled.

59. Canceled.

35

60. Canceled.

61. Canceled.

5 62. Canceled.

63. Canceled.

64. Canceled.

10

65. Canceled.

66. Canceled.

15

67. Canceled.

68. An apparatus effective at least for the reduction of oxides of nitrogen (NO_x) in a gas stream, the apparatus comprising:

a supply of source hydrocarbon;

20

a source of oxygen;

a mixer for receiving source hydrocarbon from the supply and for receiving the oxygen and for producing a mixture thereof;

a catalyst comprising a platinum group metal effective for the catalytic partial oxidation of the source hydrocarbon in the mixture to produce activated reductant therefrom;

25

a NO_x -reduction catalyst member positioned for contact with the gas stream with the activated reductant therein;

a temperature sensor for sensing the temperature of a gas stream;

at least one oxygen sensor for sensing whether such gas stream is lean; and

a control unit responsive to the sensors, for operating the apparatus to produce

30

activated reductant when the oxygen sensor indicates a lean gas stream and the temperature sensor indicates a temperature of less than about 200°C.

69. The apparatus of claim 68 wherein the control unit is configured to initiate the apparatus when the temperature sensor indicates a temperature in the range of from about 140°C to 160°C.

5 70. A method for producing an activated hydrocarbon species, comprising mixing a source hydrocarbon with oxygen and contacting with a non-catalyzed heating element at a temperature of at least about 350°C.

10 71. The method of claim 70 comprising providing the source hydrocarbon and oxygen in quantities sufficient to provide a O₂:C ratio in the range of from about 0.3:1 to 0.8:1.

 72. The method of claim 70 or claim 71 wherein the source hydrocarbon comprises diesel fuel.

15 73. The method of any one of claims 49, 50 or 51 comprising generating the activated reductant from diesel fuel and oxygen.

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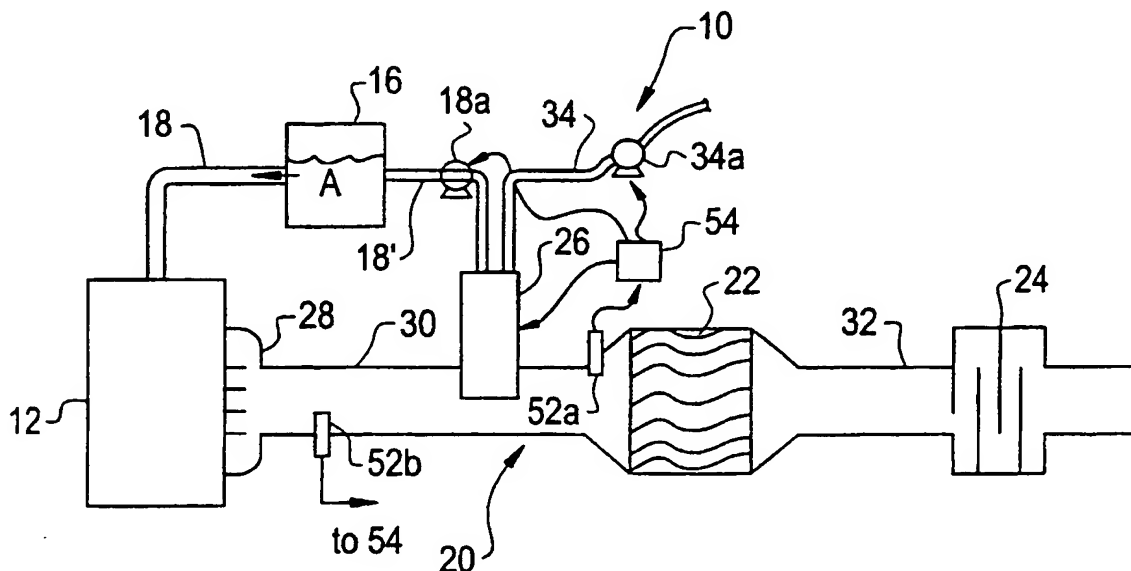
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(54) Title: METHOD AND APPARATUS TO PROVIDE REDUCTANT FOR NO_x



(57) Abstract: A method and apparatus for providing a reductant to a NO_x abatement means for a diesel engine, in which the diesel fuel is used as the reductant. The diesel fuel (A) is mixed with oxygen and is "activated", i.e., a significant portion of the diesel fuel is converted into lightweight hydrocarbon species, before being used as reductant for the NO_x. A catalytic partial oxidation (CPO) catalyst (e.g., 38) and/or a heating element (e.g., 42 or 142) can facilitate activation of the oxygen and fuel mixture. The CPO catalyst may be incorporated into injection means (26b) for the reductant. In one embodiment, a catalyzed glow plug is used to activate the reductant. Methods and apparatuses for reducing NO_x are also disclosed.



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METHOD AND APPARATUS TO PROVIDE REDUCTANT FOR NO_x

BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates to abatement of pollutants and, in particular, to an apparatus for the reduction of nitrogen oxides in a gas stream, a method for producing reductant for use in reducing nitrogen oxides and a method for operating an apparatus for the reduction of nitrogen oxides.

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Related Art

It is well-known that the exhaust of diesel engines contains noxious pollutants including carbon monoxide ("CO"), unburned hydrocarbons ("HC") and nitrogen oxides ("NO_x"). It is common practice to provide engine systems with abatement means comprising catalysts designed to convert these noxious pollutants into relatively innocuous species such as carbon dioxide, water and nitrogen. Such catalysts are well-known and may comprise oxidation catalysts to oxidize CO and HC to CO₂ and H₂O and reduction catalysts to reduce NO_x to nitrogen. Separate reduction and oxidation catalysts may be placed in the exhaust gas discharge line in series, or a "three-way conversion" catalyst may be used, for the substantially simultaneous oxidation of HC and CO and reduction of NO_x. Many catalytic materials are well-known for such purposes, for example, catalytic components that may comprise one or more platinum group metals such as platinum, palladium and rhodium, dispersed on a typically inert support material that may comprise a high surface area support such as a predominantly gamma-alumina support. The catalytic material may contain other components such as ceria and/or other base metal oxides as well as various other stabilizers and promoters. As is well-known in the art, such catalytic materials may be coated as a washcoat onto the walls of the gas flow passages of a refractory support, such as stainless steel or ceramic-like support, e.g., a cordierite support having a plurality of fine, parallel gas flow passages extending therethrough to provide a flow-through catalyst member. The abatement means may comprise a particulate trap for removing particulates from the exhaust gas stream and/or an adsorbent material. Catalysts may be used in conjunction with other abatement means, as is known in the art.

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One known expedient in the art for improving catalytic NO_x conversion is to directly inject diesel fuel into the catalyst bed as a reductant during lean engine operating conditions. However, when diesel fuel is injected into a cold catalyst, i.e., at a temperature lower than about 200°C, and/or when the exhaust gas temperature is lower than the vaporization temperature of the fuel, the efficiency and functionality of the catalyst for the reduction of NO_x is significantly reduced.

Japanese Patent 92JP-258044 of Kumagai et al for "Exhaust Emission Control Device" pertains to a NO_x-reducing catalyst mounted in an exhaust pipe. The NO_x-reducing catalyst is activated by a reducing agent (i.e., hydrocarbons). Liquid hydrocarbon fuel drawn from a fuel tank is contacted with a reforming catalyst which produces low molecular weight liquid hydrocarbon that is injected into the exhaust gas stream via an injector positioned upstream from the NO_x-reducing catalyst. This reference does not show the addition of oxygen to the reducing agent.

U.S. Patent 5,357,908 to Sung et al, dated October 25, 1994, discloses a fuel modification method and apparatus in which fuel vapors and/or liquid fuel without added oxygen are cracked by cracking catalyst bed (30) before being provided to the engine. The distillate (i.e., the cracked fuel) is used during the engine cold start period to improve (i.e., lower) the light-off activity temperature of the catalyst. The cracking catalyst bed (30) can be regenerated by flowing oxygen therethrough to burn off carbonaceous deposits and flowing the effluent into the exhaust treatment apparatus at a point upstream of the catalytic converter (22). The hydrocarbon fuel is directed away from the cracking catalyst bed during regeneration (see column 8, lines 44-50).

U.S. Patent 3,896,616 to Keith et al, dated July 29, 1975, discloses an exhaust gas treatment apparatus including an initial or warm-up catalyst and a downstream catalyst. During fuel-rich cold-start operation, oxygen is added to the exhaust gas by adding air at a point upstream from the warm-up catalyst so that it can oxidize the unburned hydrocarbons therein (see column 4, lines 3-23). The effect of adding the air under these conditions is to lower the light-off temperature of the catalyst. After the warm-up period, the warm-up catalyst is then used to reduce NO_x in the gas stream and for this purpose, additional fuel is added to the exhaust gas (see column 4, lines 24-43). The Patent discloses the preference for the use of hydrocarbon fuel reductant in the C-3 to C-12 range (see column 8, line 65 through column 9, line 3).

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In describing engine operating conditions and the composition of exhaust gases resulting therefrom, references to "rich" and "lean" operation or exhaust gases refer to the proportion of air to fuel provided to the engine and, by extension, to the proportion of unconsumed oxygen to unburned hydrocarbons in the exhaust gas. An air-fuel ratio of 14.65 (wt. basis) is the stoichiometric ratio corresponding to the combustion of a hydrocarbon fuel with an average formula $\text{CH}_{1.88}$. Fuels with different carbon/hydrogen ratios will require slightly different air-fuel ratios to produce a stoichiometric mixture. To avoid confusion in making comparisons, the Greek symbol λ has been used at times to represent the relationship of a particular air-fuel ratio to the stoichiometric ratio. The air-fuel ratio is divided by the stoichiometric ratio so that in this system $\lambda = 1$ is a stoichiometric mixture. $\lambda > 1$ is a fuel-lean mixture and $\lambda < 1$ is a fuel-rich mixture. For example, at an air-fuel ratio of 14.5, the $\lambda = 14.5/14.65 = 0.9898$.

SUMMARY OF THE INVENTION

The present invention provides an apparatus effective for generating activated reductant from a source hydrocarbon. The apparatus comprises a mixer for receiving and mixing a source hydrocarbon and oxygen and activation means for speciating the source hydrocarbon to produce activated reductant.

In one embodiment, the apparatus may comprise a mixer having inlets for receiving the source hydrocarbon and oxygen, a mixing chamber for creating a mixture of the source hydrocarbon and oxygen and an outlet for discharging activated hydrocarbon species, and also a catalyst disposed in the mixer for contact with the mixture, the catalyst being effective for activating the source hydrocarbon.

According to one aspect of the invention, the apparatus may comprise a glow plug comprising a catalyzed heating element disposed in the mixer.

In another embodiment, an apparatus according to the present invention comprises a mixer having inlets for receiving the source hydrocarbon and oxygen, a mixing chamber for creating a mixture of the source hydrocarbon and oxygen and an outlet, and also a heating element positioned to generate activated hydrocarbons from the mixture of the source hydrocarbon and oxygen. Optionally, the heating element may be disposed in the mixing chamber. In a particular embodiment, the heating element may comprise a glow plug mounted thereon with the heating element in the mixing chamber. Additionally or alternatively, a heating element may be positioned to contact the mixture discharged from the outlet of the

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mixer to generate activated hydrocarbon species therefrom. For example, the heating element may have a heater inlet connected to the mixer outlet for receiving the mixture of source hydrocarbon and oxygen and a heater outlet for discharging activated hydrocarbon species. There may be a catalyst in the heating element positioned to contact the mixture prior to
5 discharge of the activated hydrocarbon species from the heater outlet.

An apparatus according to the present invention may further comprise a temperature sensor for sensing the temperature of a gas stream and an oxygen sensor for sensing whether such gas stream is lean, and may further comprise a control unit responsive to the sensors, for initiating the apparatus when the oxygen sensor indicates a lean gas stream and the temperature
10 sensor indicates a temperature of less than 200°C. The control unit may be configured to initiate the apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C. There may be an air pump connected for delivering oxygen to the mixer and a fuel pump connected for delivering source hydrocarbon to the mixer.

According to one aspect of the invention, the apparatus may further comprise a
15 temperature sensor for sensing the temperature of the gas stream and an oxygen sensor for sensing whether the gas stream is lean. There may also be a control unit responsive to the sensors, for initiating the apparatus when the oxygen sensor indicates a lean gas stream and the temperature sensor indicates a temperature of less than 200°C, e.g., a temperature in the range of about 140°C to 160°C, wherein activating the apparatus comprises activating the air pump
20 and the fuel pump.

The present invention also provides an apparatus effective at least for the reduction of oxides of nitrogen (NO_x) in a gas stream, the apparatus comprising a supply of source hydrocarbon, a source of oxygen, an apparatus effective for generating activated reductant as described above, and a NO_x -reduction catalyst positioned for contact with the gas stream with
25 the activated reductant therein.

The present invention also provides a method for producing an activated hydrocarbon species, comprising mixing a source hydrocarbon with oxygen and subjecting the mixture to activating conditions. In a particular embodiment of this method, the source hydrocarbon may comprise diesel fuel.

30 The method may comprise contacting the mixture with a catalytic material effective to facilitate speciation of the source hydrocarbon. It may comprise heating the mixture to a temperature of at least about 350°C, optionally without a catalyst, or contacting the mixture at a

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temperature lower than 350°C, e.g., in the range of from about 200°C to 340°C, and contacting the mixture with a catalyst effective to facilitate speciation at such lower temperature.

The present invention also provides an activated hydrocarbon reductant produced by the method comprising mixing a source hydrocarbon with oxygen and subjecting the mixture to activating conditions. In a particular embodiment, the source hydrocarbon may comprise diesel fuel.

The invention also relates to a method for reducing oxides of nitrogen (NO_x) in a lean gas stream. The method comprises creating a fuel-oxygen mixture by mixing diesel fuel vapor with oxygen, subjecting the fuel-oxygen mixture to activating conditions to create an activated diesel reductant, mixing the activated diesel reductant into the gas stream and contacting the gas stream with the activated diesel reductant therein with a NO_x -reduction catalyst. The method may comprise mixing the activated diesel reductant with the gas stream at a temperature below 200°C, e.g., at a temperature in the range of about 140°C to 200°C or in the range of about 140°C to 160°C.

Furthermore, this invention provides a method of operating an apparatus for the reduction of NO_x in a lean gas stream. This method comprises flowing the gas stream into contact with a NO_x -reduction catalyst, sensing the temperature of the gas stream contacting the NO_x -reduction catalyst and introducing activated diesel reductant into the gas stream for contact with the NO_x -reduction catalyst when the temperature of the gas stream is in the range of 140°C to 200°C, e.g., in the range of 140°C to 160°C.

This invention also presents an improved glow plug comprising a heating element extending from a plug body, the improvement comprising that a coating of catalytic material is carried on the heating element, the catalytic material being effective to facilitate the speciation of a source hydrocarbon. There may be an anchor layer on the heating element between the heating element and the catalytic material, and the anchor layer may comprise a metal that is thermally sprayed onto the heating element of the glow plug. For example, the anchor layer may be electric arc sprayed onto the heating element of the glow plug. The anchor layer may be deposited on the heating element by electric arc spraying a metal feedstock selected from the group consisting of nickel, Ni/Al, Ni/Cr, Ni/Cr/Al/Y, Co/Cr, Co/Cr/Al/Y, Co/Ni/Cr/Al/Y, Fe/Al, Fe/Cr, Fe/Cr/Al, Fe/Cr/Al/Y, Fe/Ni/Al, Fe/Ni/Cr, 300 series stainless steels, 400 series stainless steels, and mixtures of two or more thereof. In a particular embodiment, the anchor layer may comprise nickel and aluminum. Optionally, the aluminum may comprise from about

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3 to 10 percent, e.g., from about 4 to 6 percent, of the combined weights of nickel and aluminum in the anchor layer. Typically, the catalytic material is deposited on the anchor layer and may comprise a refractory metal oxide support on which one or more catalytic metal components are dispersed.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1A, 1B, 1C, 2 and 3A and 3B are chromatogram plots of molecular weight distributions of hydrocarbon species in diesel fuel vapor samples, generated by a gas chromatograph analyzer;

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Figure 4 is a schematic diagram of a typical diesel engine system including an exhaust treatment apparatus in accordance with the present invention; and

Figures 5A, 5B, 6, 7A and 7B are schematic diagrams showing various embodiments of exhaust treatment apparatuses in accordance with the present invention.

15

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS THEREOF

The present invention relates to abatement of pollutants and, in particular, to an apparatus for the reduction of nitrogen oxides in a gas stream, a method for producing reductant for use in reducing nitrogen oxides and a method for operating an apparatus for the reduction of nitrogen oxides. The invention is especially pertinent to the reduction of NO_x from lean exhaust gases. The present invention provides for the activation of a source hydrocarbon to provide a reductant, referred to herein and in the claims as "activated reductant", that is more reactive as a reductant for the NO_x than the source hydrocarbon. The superior activity of activated reductant relative to the source hydrocarbon is believed to be due to the generation from the source hydrocarbon of lower molecular weight hydrocarbon species which render the fuel vapors more reactive than the source hydrocarbon. For this reason, activation of the source hydrocarbon is also sometimes referred to herein as "speciation" or "cracking" of the source hydrocarbon. In particular embodiments of the present invention, the source hydrocarbon comprises diesel fuel and the activated reductant is sometimes referred to herein as "activated diesel reductant", which is believed to contain a significant proportion of low molecular weight hydrocarbon species, e.g., C-10 or smaller (e.g., C-3, C-4).

30

The use of activated reductant permits the effective use of the catalyst for the reduction of NO_x at temperatures lower than those permitted by the source hydrocarbon. When the reductant is non-activated diesel fuel vapor, the effectiveness threshold temperature for a conventional lean NO_x -reduction catalyst is about 200°C . Below the threshold temperature, the reduction reaction is inadequate and the non-activated diesel fuel vapors condense on the catalyst and deactivate it. The use of activated diesel reductant facilitates the reduction reaction, lowering the effectiveness threshold temperature below 200°C , e.g., from about 140°C to 200°C and/or from about 140°C to 160°C . In addition, the activated diesel reductant, being of lower molecular weight and therefore generally more volatile than non-activated diesel fuel vapors, does not exhibit a condensation problem at those temperatures as does the source hydrocarbon. Naturally, the present invention may optionally be practiced at the temperature range in which non-activated reductant is acceptable as well, i.e., at 200°C or higher.

One feature of the invention relates to the Applicants' finding that speciation is greatly facilitated when a source hydrocarbon, e.g., diesel fuel vapor, is mixed with a limited amount of oxygen and the mixture is exposed to activating conditions, presumably because the source hydrocarbon is partially oxidized as it is cracked into hydrocarbons of lesser molecular weight. The oxygen may be included in air mixed with the fuel or may be provided from any other suitable source. Preferably, the proportion of oxygen in the mixture relative to the quantity of carbon atoms corresponds to an $\text{O}_2:\text{C}$ ratio of at least about 0.3:1 (i.e., an oxygen-to-carbon atomic ratio in the mixture of at least about 0.6:1), since it is believed that lesser amounts of oxygen will lead to coking of the source hydrocarbon that will foul the apparatus. It is believed that a loss of efficiency in the production of light hydrocarbons (excluding CO_2) is exhibited as the ratio increases above 0.5:1, which is a preferred $\text{O}_2:\text{C}$ ratio, but acceptable production of light hydrocarbons can be obtained up to an $\text{O}_2:\text{C}$ ratio of about 0.8:1. Practical working ranges for the $\text{O}_2:\text{C}$ ratio include ratios in the range of from about 0.3:1 to 0.6:1, from about 0.35:1 to 0.5:1, from about 0.35:1 to 0.45:1, and from about 0.42:1 to 0.5:1.

In accordance with this invention, the oxygen-hydrocarbon mixture is subjected to activating conditions, which includes heating the mixture to a speciation temperature, i.e., a temperature at which speciation, e.g., partial oxidation, occurs. The speciation temperature may be at least about 350°C in the absence of a catalyst, but may be lower than 350°C when subjecting the mixture to activating conditions includes contacting the mixture with a catalyst effective to facilitate speciation of the fuel, i.e., a speciation catalyst. The speciation catalyst

may comprise a partial oxidation catalyst, i.e., a catalyst that facilitates the partial oxidation of the source hydrocarbon. In the presence of such a catalyst, the speciation temperature may be as low as about 200°C, i.e., speciation may occur at temperatures of 200°C or greater, e.g., at temperatures of from about 200°C to 350°C, e.g., from about 200°C to 340°C or from about
5 200°C to 300°C.

Another feature of the invention relates to hydrocarbon activation apparatuses or activated reductant means for mixing a source hydrocarbon such as diesel fuel with oxygen and speciating the source hydrocarbon by subjecting the mixture to activating conditions to produce an activated reductant. Such an apparatus is preferably configured for use as an exhaust
10 treatment apparatus through which an exhaust gas stream flows for treatment. The oxygen-source hydrocarbon mixture may be activated either before or after it is provided to the exhaust gas stream. For example, the activated reductant means may include a mixer such as a fuel injector for mixing the source hydrocarbon with oxygen. The activated reductant means may comprise an activating means such as a heat source for heating and/or vaporizing the source
15 hydrocarbon and/or otherwise heating the oxygen-hydrocarbon mixture in any manner effective to raise the temperature of the mixture to a speciation temperature. The heat source may comprise, e.g., an electric heating element or a glow plug. Alternatively, or in addition to the heat source, the activating means may comprise a catalyst that facilitates the activation of the reductant by catalyzing or facilitating speciation of the source hydrocarbon. For example, a
20 catalyst member comprising a carrier coated with catalytic material can be mounted in the injector or for contact with the oxygen-hydrocarbon mixture created therein. There may be a heat source for heating the catalyst, e.g., there may be a heating element for heating a catalytic material, e.g., for heating a catalyst member. In a particular embodiment, the activating means may comprise a catalyzed glow plug.

25 According to particular embodiments of the invention in which the NO_x is present in the exhaust gas stream of a diesel engine and wherein the source hydrocarbon comprises diesel fuel, an exhaust gas treatment apparatus may comprise an activated reductant means comprising a fuel injector connected to an exhaust pipe for the engine, for mixing the fuel with oxygen. There may be a coupling fixture or holder to couple the fuel injector to the exhaust pipe and to
30 accommodate activating means such as a heating element and/or a catalyst to facilitate speciation of the fuel exiting the injector before it enters the exhaust pipe. Alternatively, the injector may be modified to accommodate the activating means. In yet another embodiment, a

conventional injector can be used to form the oxygen-diesel fuel mixture and inject it into the exhaust gas pipe, and the exhaust pipe may be modified to accommodate the activating means and to flow the mixture into contact therewith. Optionally, the mixture may be isolated from the exhaust gas until after the reductant is activated, e.g., by means of a conduit within the exhaust pipe within which the activating means is disposed and through which the mixture flows to contact the activating means, after which it leaves the conduit and is mixed with the exhaust gas. By disposing the activating means in a holder for the injector and/or within the exhaust gas pipe and/or within the injector itself, the Applicants have provided a means for activating the reductant without adding significantly to the spatial demands of a conventional NO_x abatement system or a conventional exhaust gas treatment apparatus.

The Applicants performed experiments using a gas chromatograph ("gc") to determine conditions that favor "activation" or "speciation" of diesel fuel vapor hydrocarbons and that can be replicated using the activated reductant means described herein. In these experiments, a 1 centimeter (cm) x 2.5 cm inert catalyst carrier core was loaded into a portable reactor that was attached to the front of a gas chromatograph with graphite ferrules. In some tests the carrier core was uncoated; in others, the core carried a washcoat of a catalytic material effective to facilitate speciation of the fuel, i.e., to facilitate catalytic partial oxidation (CPO); and in still others the CPO material was tested in powder form.

In a typical test procedure, the reactor and all the interface lines were stabilized at 300°C for at least 1 hour. In various trials, helium or zero grade air at 10 psi was introduced into the injection system in front of the reactor. In each test, a 10 microliter aliquot of No. 2 diesel fuel was injected through a septum into the flowing helium or air at a point upstream from the carrier core. The helium or air supply was turned off after a 12 second injection. The space velocity through the carrier core was typically in the range of 250 to 500 hr⁻¹. A gc analysis was performed on the effluent from the uncoated or coated carrier core. The formation of "activated" reductant was observed as the detection of an increase in the proportion of lightweight hydrocarbons, i.e., C-10 or less, preferably C-3 and C-4, in the sample, some of which may have been oxygenated (i.e., in the form of alcohols, aldehydes, etc.).

Some tests were performed using an uncoated or "blank" carrier core and helium. The results of these tests showed that heating diesel fuel vapors in an inert atmosphere, e.g., in mixture with helium, did not cause significant speciation, i.e., activation, of the diesel fuel hydrocarbons, i.e., there was no significant increase in the proportion of lightweight

hydrocarbons, even when heated to temperatures as high as 475°C. However, the Applicants have found that when diesel fuel vapors are mixed with limited amounts of oxygen, which may be supplied by air or any other suitable source, speciation can be induced by exposing the mixture to activating conditions. The diesel fuel reductant thus becomes "activated", i.e., a significant portion of the diesel fuel is converted into lightweight hydrocarbon species, i.e., C-10 or less. Activating conditions have been found to include heating the mixture to a temperature of at least about 350°C in the absence of a catalyst. Activating conditions also include contacting the oxygen-fuel mixture with a catalytic material effective to facilitate speciation, e.g., the catalytic partial oxidation ("CPO"), at temperatures that may optionally be lower than 350°C but typically at least about 200°C. Materials suitable for use as CPO catalytic materials are described below.

To illustrate the findings and results realized in accordance with the present invention, the chromatogram of Figure 1A shows the results of a gas chromatograph analysis of vaporized diesel fuel that was mixed with helium (an inert gas) instead of oxygen, heated to 350°C and flowed through a blank core, while Figure 1B shows the results obtained when vaporized diesel fuel and helium with no added oxygen were flowed over a catalyst at 450°C. In these Figures and in Figures 1C, 2, 3A and 3B, the horizontal axis indicates retention time (in minutes) and the vertical axis indicates a response voltage (in millivolts) derived from a detector, as is well-known in the art. Figures 1A and 1B show that no significant cracking or speciation occurs in an inert atmosphere in the absence of a catalyst, even at high temperature. These results show that the disclosure of Japanese patent document 92JP-258044 discussed above is not enabling with respect to the generation of activated hydrocarbon reductant from a diesel fuel source hydrocarbon.

Figure 1C shows the results of a mixture of the vaporized diesel fuel with air (as a source of oxygen) heated to 340°C and flowed through a blank core. The outcome was similar to that of Figures 1A and 1B, and indicates that even in the presence of air, a temperature of 340°C is not adequate to generate significant speciation in the absence of a catalyst.

Figure 2 presents the non-catalytic, thermal cracking results obtained by flowing the air-fuel mixture over a blank core at 350°C, and shows by virtue of the reduced spikes in the 5 minute to 20 minute range and the strong spike at about two minutes that a significant proportion of the diesel fuel hydrocarbons were cracked into lightweight species.

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Test data obtained from the air-fuel mixture revealed that at temperatures below 350°C, the proportion of light hydrocarbons (smaller than C-10) in the effluent, excluding carbon dioxide, was in the range of 0.3 to 0.4 percent. As the temperature rises from 350°C to 450°C, the proportion of light hydrocarbons (HC) increases as

5 shown in the following TABLE I.

TABLE I

Air-Fuel Mixture		% Light HC (<C-10)
<u>Injector Temperature °C</u>		<u>(Excluding CO₂)</u>
10	300	0.4%
	325	0.4%
	340	0.3%
	340	0.3%
	345	0.3%
15	350	5.7%
	350	5.8%
	375	26.8%
	400	34.7%
	450	36.2%

20

The data of TABLE I illustrate that significant speciation occurs in an air-fuel mixture at temperatures of at least about 350°C, with a significant increase between 350°C and 375°C.

Other gc tests show that the use of a CPO catalyst facilitates speciation at temperatures lower than that required for non-catalytic speciation, i.e., lower than 350°C, e.g., to 300°C. In
25 these tests, catalysts were used in two forms; in powder form, in which case the air-fuel mixture was flowed through a powder reactor having a volume of about 0.125 cubic centimeters (cc) and containing about 100 milligrams of catalytic material powder, and in the form of a coating on the catalyst carrier core having a one centimeter (cm) diameter and a volume of about 1.96 cc at a coating weight of about 1.8 grams/cc.

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A variety of catalytic components was found to be effective for use in CPO catalytic materials, including supported precious metals, rare earth metal compounds, transition metal compounds and zeolite-based materials, and these will generally be effective either alone or in

combination. The following Examples present data obtained from the use of supported precious metal-type catalysts, specifically, catalytic materials comprising a catalytic component comprising rhodium dispersed on alumina. It will be understood by one of ordinary skill in the art, however, that other supported catalytic components, e.g., other platinum group metals, may be used effectively in this way, and that they may be supported on any of a variety of refractory inorganic oxide support materials.

CPO catalytic materials comprising supported catalytic components can be prepared by procedures well known in the art, e.g., by dispersing a compound and/or complex of any catalytically active component, e.g., one or more platinum group metal compounds or complexes, onto a relatively inert bulk support material. The compounds or complexes of one or more catalytic components may be dissolved or suspended in any liquid which will wet or impregnate the support material, which does not adversely react with other components of the catalytic material and which is capable of being removed from the catalyst by volatilization or decomposition upon heating and/or the application of a vacuum. Generally, both from the point of view of economics and environmental aspects, aqueous solutions of soluble compounds or complexes are preferred. For example, suitable water-soluble platinum group metal compounds are chloroplatinic acid, amine solubilized platinum hydroxide, rhodium chloride, rhodium nitrate, hexamine rhodium chloride, palladium nitrate or palladium chloride, etc. The compound-containing liquid is impregnated into the pores of the bulk support particles of the catalyst, and the impregnated material is dried and preferably calcined to remove the liquid and bind the platinum group metal into the support material. In some cases, the completion of removal of the liquid (which may be present as, e.g., water of crystallization) may not occur until the catalyst is placed into use and subjected to the high temperature exhaust gas. During the calcination step, or at least during the initial phase of use of the catalyst, such compounds are converted into a catalytically active form of the platinum group metal or a compound thereof. An analogous approach can be taken to incorporate the other components into the catalytic material. Optionally, the inert support materials may be omitted and the catalytic material may consist essentially of the catalytic component deposited directly on the sprayed carrier substrate by conventional methods.

Suitable support materials for the catalytic component include alumina, silica, titania, silica-alumina, aluminosilicates, aluminum-zirconium oxide, aluminum-chromium oxide, etc. Such materials are preferably used in their high surface area forms. For example, gamma-

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alumina is preferred over alpha-alumina. It is known to stabilize high surface area support materials by impregnating the material with a stabilizer species. For example, gamma-alumina can be stabilized against thermal degradation by impregnating the material with a solution of a cerium compound and then calcining the impregnated material to remove the solvent and
5 convert the cerium compound to a cerium oxide. The stabilizing species may be present in an amount of from about, e.g., 5 percent by weight of the support material.

As is known in the art, modifiers may optionally be employed in activated-alumina containing catalyst compositions. Among such modifiers are thermal stabilizers which serve to retard undesirable alumina phase transitions (e.g., gamma- to alpha-alumina) at elevated
10 temperatures which the catalyst may encounter in use. The thermal stabilizers may be any known stabilizer or combination of stabilizers such as, for example, one or more rare earth metal oxides, silicon dioxide, oxides of Group IVB metals (zirconium, hafnium and titanium) or one or more alkaline earth metal oxides. Other modifiers such as oxides of chromium, iron and nickel, or their precursors, may also be employed. Some modifiers may serve more than one
15 function, e.g., may serve as both a thermal stabilizer and a catalytic promoter. These materials, or precursors thereof, may be impregnated from a solution or liquid dispersion into the activated alumina particles either before or after the particles are formed into an adherent coating on the carrier substrate. (As used herein and in the claims, a "precursor", whether of a thermal stabilizer, other modifier or other component, is a compound, complex or the like which, upon
20 calcining or upon use of the catalyst, will decompose or otherwise be converted into, respectively, a thermal stabilizer, other modifier or component.) The presence of one or more of these metal oxide stabilizers tends to retard the phase transition of high surface area aluminas such as gamma- and eta-alumina to alpha-alumina, which is a low surface area alumina. The retardation of such phase transformation tends to prevent or reduce the occlusion of the catalytic
25 metal component by the alumina with the consequent decrease of catalytic activity. The amount of metal oxide stabilizer combined with the alumina may be from about 0.05 to 30 weight percent, preferably from about 0.1 to 25 weight percent, based on the total weight of the combined alumina, stabilizer and catalytic component. Alkaline earth metal oxides which may be used to stabilize activated alumina are oxides of barium, strontium, calcium and magnesium.
30 Among the rare earth metal oxides which may be similarly employed in the catalyst are oxides of cerium, lanthanum, neodymium, praseodymium and mixtures thereof, including the commercially available mixtures of rare earth metal oxides.

The zeolitic catalysts that may be used as CPO catalysts in the practice of this invention may be of the type that have cracking properties for long-chain and aromatic hydrocarbons, and so may crack long-chain hydrocarbons in the reductant.

Zeolites that are known to be useful for cracking long-chain hydrocarbons include the following structural types: faujasites, pentasiles, mordenites, ZSM 12, zeolite β , zeolite L, zeolite Ω , ZSM 22, ZSM 23, ZSM 48, EU-1 and the like. The zeolite of the pentasile type may exhibit a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 25 to 2,000, e.g., between 40 and 600. Zeolites are crystalline aluminosilicates which are made up of a network of SiO_4 or M^2O_4 tetrahedrons and may be characterized by the general formula (I)



wherein

M^1 is an equivalent of an exchangeable cation, its quantity corresponding to the M^2 quantity;

M^2 is a trivalent element which together with the Is forms the oxidic framework of the zeolite;

n/m is the $\text{SiO}_2/\text{M}^2\text{O}_2$ ratio;

q is the amount of adsorbed water.

The individual tetrahedrons are linked at the apices of the tetrahedrons via oxygen bonds and form a three-dimensional network which is regularly traversed by channels and hollow spaces. Various zeolite structures differ in their arrangement and size of the channels and hollow spaces and in their compositions. As a counterbalance of the negative charge of a zeolite lattice, which is accounted for by the M^2 content, exchangeable cations are deposited. The adsorbed aqueous phase qH_2O is reversibly removable without the framework losing its structure.

M^2 is often aluminum but can be partially or completely substituted by other trivalent elements.

A detailed description of zeolites is given, e.g., in the monograph by D.W. Breck *"Zeolite Molecular Sieves, Structure, Chemistry and Use"*, J. Wiley & Sons, New York, 1974.

A further description, in particular of the SiO_2 -rich zeolites which are of interest for catalytic uses, is given in the monograph by P.A. Jacobs and J.A. Martens *"Synthesis of High-Silica*

Aluminosilicate Zeolite", Studies in Surface Science and Catalysis, Vol. 33, Ed. B. Delmon and J.T. Yates, Elsevier, Amsterdam-Oxford-New York-Tokyo, 1987.

Some zeolites of the kind described above are disclosed in European Patent Application 92 10 2161.4(A1). In the zeolites described therein, M^2 is one or several elements from the group Al, B, Ga, In, Fe, Cr, V, As and Sb, preferably one or several elements of the group Al, B, Ga and Fe. It is further taught that the aforementioned zeolites could contain Li, Na, K, Rb, Cd, Cs, Mg, Ca, Sr, Ba and the transition metal cations such as B, Cr, Mn, Fe, Co, Ni, Cu, V, Nb, Mo, Ru, Rh, Pd, Ag, Ta, W, Zn, Re, Pt as exchangeable cations M^1 . Similarly useful are cations of the rare earth group and protons. Zeolites in which at least part of the metal cations, preferably 50-100% thereof, have been replaced by hydrogen ions (H^+), i.e., acid zeolites, are preferred. It is particularly preferred that 80-100% of all metal cations originally present be replaced by H^+ .

The acidic H^+ forms of the zeolites may be obtained by exchanging ammonium ions for metal ions and by calcination of the thus exchanged zeolites. Repetition of the exchange procedure and subsequent calcination under the defined conditions leads to so-called ultrastable zeolites in the zeolites of the faujasite type which become thermically and hydrothermally more stable by this dealumination process. A further possibility to obtain SiO_2 -rich zeolites of the faujasite type is to specifically treat the water-free zeolites with $SiCl_4$ at elevated temperatures ($\geq 150^\circ C$). Aluminum is removed and at the same time silicon is introduced into the lattice. Treatment with ammonium hexafluorosilicate under certain conditions also results in SiO_2 -rich faujasites.

A further possibility for the exchange of protons in the case of zeolites that exhibit a SiO_2/Al_2O_3 ratio of at least 5:1 is to carry out the process with mineral acids.

It is known that the ion exchange with trivalent rare earth metal ions, individually and/or in admixture which preferably can be rich in lanthanum or cerium, leads to acidic centers, particularly in the case of faujasites, and that an exchange of aluminum for transition metal cations leads to acidic centers.

The above-described zeolites with acidic centers have the catalytic property of cracking hydrocarbons, i.e., of cleaving them into smaller fragments.

For purposes of the following Examples, CPO catalysts comprising rhodium dispersed on alumina were prepared. Typically, alumina powder having a surface area of about 90 square meters per gram was impregnated with a rhodium nitrate solution to 80 percent of incipient

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wetness. The rhodium nitrate solution was diluted to give a desired metal concentration by weight of rhodium plus alumina. The impregnated powder was milled with acetic acid in an amount of about 2 percent by weight of the material to produce a slurry. No other catalytically active species were added to the alumina. For purposes of some of the following tests, the slurry was coated onto the catalyst carrier core, which was then dried and calcined. In other tests, the slurry was simply dried and calcined for use in powder form in a powder reactor. In tests of exhaust gas treatment apparatuses demonstrating the present invention, the slurry was coated onto a catalyst carrier core or onto the surface of a glow plug, as appropriate.

Figures 3A and 3B show results obtained when a fuel-air mixture was flowed at 300°C through catalyst carrier cores coated with the rhodium-on-alumina catalyst material described above. Figure 3A shows the results obtained using the 0.3 weight percent rhodium catalytic material while Figure 3B shows the results obtained using the 3 percent rhodium catalytic material. Both Figures 3A and 3B show that significant speciation of the diesel fuel occurred.

A comparison of results obtained by using a catalytic material as a coating on a carrier core as opposed to being tested in powder form is provided in the following TABLE II.

TABLE II

Catalytic			
<u>Material</u>	<u>Form</u>	<u>% Light HC</u>	
3% Rh/alumina	core	71%	
3% Rh/alumina	powder	7%	
0.5% Rh/alumina	core	7%	
0.5% Rh/alumina	powder	0.8%	

The data of TABLE II indicate that about ten times the percent of light hydrocarbons (i.e., C-10 or smaller) was formed over a catalyst-coated core relative to a powdered catalyst. The difference between the powder catalyst and coated core is believed to be due at least in part to the fact that the space velocity of gas through the powder reactor was 16 times the velocity through the core reactor.

Figure 4 is a system block diagram of a typical diesel engine system comprising diesel engine 12, fuel tank 16 and a primary fuel line 18 connecting fuel tank 16 to diesel engine 12 to provide diesel fuel A thereto. Typically, a fuel pump (not shown) is utilized to

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facilitate the provision of diesel fuel A to engine 12 through fuel line 18. Engine 12 generates an exhaust gas stream that contains NO_x. Exhaust apparatus 20 defines a flow path for emissions of engine 12 from the engine into an exhaust manifold 28 and then into a conduit such as an exhaust pipe 30. The flow path continues through a conventional NO_x abatement catalyst 22, pipe 32 and a muffler 24, from which treated exhaust gases are discharged. The NO_x abatement catalyst may comprise, e.g., a honeycomb carrier coated with catalytic material effective at least for the reduction of NO_x. One suitable type of NO_x abatement catalyst is well-known in the art as a three-way catalyst (TWC catalyst). Such catalysts are known for their ability to substantially simultaneously catalyze the oxidation of hydrocarbons and carbon monoxide and the reduction of NO_x under generally stoichiometric conditions. Such catalysts are prepared by dispersing a platinum group metal, e.g., one or more platinum group metal compounds or complexes onto a relatively inert bulk support material. The ingredients and preparation procedure of such TWC catalysts is well-known in the art and is substantially described above in reference to platinum group metal-containing CPO catalyst materials, and so need not be repeated here.

In other embodiments, the NO_x abatement catalyst for use with the present invention may be specially formulated as a so-called lean NO_x catalyst. Such catalysts are known to comprise a catalyst and a NO_x sorbent. The NO_x sorbent stores NO_x during periods of lean (oxygen-rich) operation, and releases the stored NO_x during the rich (relatively fuel-rich) periods of operation. During periods of rich operation, the catalyst component of the catalyst/NO_x sorbent promotes the reduction of NO_x to nitrogen by reaction of NO_x (including NO_x released from the NO_x sorbent) with HC, CO and/or hydrogen present in the exhaust.

The use of NO_x storage (sorbent) components including alkaline earth metal oxides, such as oxides of Ca, Sr and Ba, alkali metal oxides such as oxides of K, Na, Li and Cs, and rare earth metal oxides such as oxides of Ce, La, Pr and Nd in combination with precious metal catalysts such as platinum dispersed on an alumina support, is known, as shown for example, at column 4, lines 19-25, of U.S. Patent 5,473,887 of S. Takeshima et al, issued on December 12, 1995 which is incorporated herein by reference, for background information. At column 4, lines 53-57, an exemplary composition is described as containing barium (an alkaline earth metal) and a platinum catalyst. The publication *Environmental Catalysts For A Better World And Life*, Proceedings of the 1st World Congress at Pisa, Italy, May 1-5, 1995, published by the Societa Chimica Italiana of Rome, Italy has, at pages 45-48 of the publication, an article entitled

"The New Concept 3-Way Catalyst For Automotive Lean-Burn Engine Storage and Reduction Catalyst", by Takahashi et al (below referred to as "the Takahashi et al paper"). This article discloses the preparation of catalysts of the type described in the above-mentioned Takeshima et al U.S. Patent 5,473,887 by impregnating precious metals, mainly platinum, and various
5 alkaline and alkaline earth metal oxides, mainly barium oxide, and rare earth oxides on refractory metal oxide supports, mainly alumina, and using these catalysts for NO_x purification of actual and simulated exhaust gases alternately under oxidizing (lean) and reducing (rich or stoichiometric) conditions. The conclusion is drawn in the last sentence on page 46, that NO_x was stored in the catalyst under oxidizing conditions and that the stored NO_x was then reduced
10 to nitrogen under stoichiometric and reducing conditions. Another suitable lean NO_x catalyst is described in U.S. Patent 5,451,558, "Process For the Reaction and Absorption of Gaseous Air Pollutants, Apparatus Therefor and Method of Making the Same", issued on September 19, 1995 to L. Campbell et al, which discloses a catalytic material for the reduction of NO_x in combustion exhaust, e.g., from a gas turbine in a power generating stack. The material
15 comprises an oxidation species and an adsorbent species. The oxidation species may comprise various metals including platinum group metals such as platinum, palladium or rhodium (see column 3, line 67, through column 4, line 3). The adsorbent species may comprise an alkali or alkaline earth metal carbonate, bicarbonate or hydroxide, and carbonates, especially sodium carbonate, potassium carbonate or calcium carbonate, are preferred. (See column 4, lines 24-
20 31.) The catalytic material is applied by coating the carrier with, e.g., platinum-coated alumina and then wetting the alumina with an alkali or alkaline earth metal carbonate solution, and then drying the wetted alumina (see column 5, line 9, through column 6, line 12). The use of a metal monolith support for the material is suggested at column 5, lines 48-58. Finally, U.S. Patent 5,874,057, "Lean NO_x Catalyst/Trap Method", issued on February 23, 1999 to M. Deeba et al,
25 discloses a method of NO_x abatement utilizing a composition comprising a NO_x abatement catalyst comprising platinum and, optionally, at least one other platinum group metal catalyst which is kept segregated from a NO_x sorbent material. The NO_x sorbent material may be one or more of oxides, carbonates, hydroxides and mixed oxides of one or more of various alkali metals including lithium, sodium and potassium, and alkaline earth metals including
30 magnesium, calcium, strontium and barium. As set forth at column 6, line 18 et seq of the '057 Patent, a platinum catalytic component is deemed to be essential and the utilization of the NO_x sorbent material in bulk form is taught as being advantageous. The '057 Patent also teaches the

optional use of ceria, for example, bulk ceria (ceria in fine particulate form), as a component of the composition. See column 3, lines 43-44. Any of the foregoing NO_x abatement catalysts and/or any others known in the art, may be used with the present invention.

In accordance with the present invention, exhaust apparatus 20 comprises an activated
5 reductant means 26. Secondary fuel line 18' connects fuel tank 16 to an inlet to activated reductant means 26 to provide a source of diesel fuel A thereto by means of pump 18a. Optionally, secondary fuel line 18' may branch off primary fuel line 18. Air inlet line 34 provides air or another source of oxygen to the activated reductant means 26 by means of an air pump 34a. The activated reductant means subjects a mixture of vapors of the diesel fuel with
10 the oxygen source and subjects the air-fuel mixture to activating conditions to produce activated diesel reductant and introduces the activated reductant into the conduit, i.e., into the exhaust gas stream, to provide reductant for the reduction of NO_x at NO_x abatement catalyst 22.

To make the operation of exhaust apparatus 20 responsive to changing conditions, exhaust apparatus 20 may also include a temperature sensor 52 mounted in exhaust pipe 30 at a
15 point suitable for the measurement of the temperature of exhaust gases entering NO_x abatement catalyst 22. There may be a control unit 54 that is responsive to sensor 52a and optionally to at least one other sensor (not shown) that detects NO_x in the gas stream and/or operating conditions under which NO_x is expected to be produced optionally including, e.g., sensing whether the exhaust gas is lean (i.e., $\lambda < 1$) (e.g., sensor 52b) or is being produced under lean
20 operating conditions. The control unit 54 is configured so that if sensors indicate that the exhaust gas entering NO_x abatement catalyst 22 is lean and is at a temperature below 200°C it may operate the supply of source hydrocarbons and the oxygen source (e.g., it may initiate pumps 18a and 34a) and also operate the activated reductant means. By providing activated diesel reductant at such temperatures, condensation of reductant on catalyst 22 as would occur
25 with unactivated diesel reductant is avoided and the activity and durability of NO_x abatement catalyst 22 is enhanced. When the lean exhaust gas temperature is 200°C or higher, the operation of the activated reductant means may optionally be stopped but the operation of the supply of source hydrocarbons and of the oxygen source may optionally continue because at such higher temperatures adequate NO_x conversion can be achieved with unactivated diesel
30 reductant. The exhaust gas treatment apparatus of the present invention treats NO_x over a broader temperature range than conventional NO_x abatement systems by providing activated reductant when the temperature of the exhaust gas is below about 200°C.

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Exhaust apparatus 20 may optionally comprise other abatement means (not shown), e.g., an oxidation catalyst, particulate trap, etc., that may be disposed in the flow path between the engine and muffler 24 to abate other pollutants in the exhaust gas, but preferably not between the activated reductant means at 26 and NO_x abatement catalyst 22.

5 A representative embodiment of an exhaust treatment apparatus as described above with regard to Figure 4 is seen in an exhaust treatment apparatus 20a, Figure 5A, in which the activated reductant means comprises a mixer that comprises a fuel injector 26a which is dimensioned and configured to receive diesel fuel and air via fuel line 18' and air inlet line 34, respectively, and to mix therein the air and fuel. As indicated above, a fuel pump may be
10 situated in line 18' to provide suitable pressure for injector 26a. If the vehicle is equipped with air brakes, air inlet line 34 may draw air therefrom. Otherwise, the vehicle may be equipped with an air pump 34a (Figure 4) specifically configured to provide air to injector 26a. Fuel injector 26a may be a conventional fuel injector that has been modified to accommodate an activating means comprising a glow plug 36 that extends into the discharge chamber. Glow
15 plug 36 may be a conventional electrically-heated glow plug and may serve to generate activating conditions in the mixer by heating the air-fuel mixture to a temperature at which the diesel fuel will undergo speciation, i.e., so that low molecular weight hydrocarbon species are produced, yielding activated diesel reductant that is more reactive for the reduction of NO_x than the diesel fuel entering injector 26a. The heating of glow plug 36 may be controlled by the
20 control unit 54 in response to input from the temperature sensor 52. When sensors associated with the engine or positioned in the exhaust gas stream indicate that the exhaust gas stream is lean and contains a significant quantity of NO_x, the control unit 54 may initiate one or both of fuel pump 18a and air pump 34a to provide a suitable amount of diesel fuel reductant to NO_x abatement catalyst 22. If the temperature of exhaust gas entering NO_x abatement catalyst 22 at
25 that time is below about 200°C, the control unit 54 may also initiate the heating of glow plug 36 so that the reductant introduced into the NO_x-containing gas stream comprises an activated reductant in accordance with the present invention. The activated diesel reductant vents from a discharge chamber in injector 26a and is thus introduced into the exhaust gas stream in pipe 30 to provide reductant for NO_x at NO_x abatement catalyst 22.

30 Figure 5B provides a schematic cross-sectional view of a portion of a particular embodiment of an apparatus generally similar to that of Figure 5A, the engine, fuel source, air source and the NO_x abatement catalyst being omitted to simplify the drawing. The exhaust gas

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treatment apparatus in Figure 5B comprises a mixer 126 that comprises a conventional fuel injector 126a mounted in a holder 50 which also defines a conduit 50c that provides fluid flow communication between the fuel injector outlet and the interior of the exhaust pipe 30. Holder 50 defines a fuel inlet 118 that communicates with the fuel inlet 126b of injector 126a and which is dimensioned and configured for connection to a supply of source hydrocarbon, e.g., to receive a fuel line such as fuel line 18' (Figure 5A). Holder 50 also defines an air inlet 134 that is dimensioned and configured for connection to a supply of oxygen, e.g., to receive an air inlet line such as line 34 (Figure 5A) so that the fuel dispersed by injector 126a via injector outlet 126c can be mixed with air or another source of oxygen in conduit 50c. Holder 50 is further configured to receive a heat source comprising a glow plug 36 that is positioned in conduit 50c to heat the air-fuel mixture to its speciation temperature before the mixture is introduced into exhaust pipe 30. A coupling portion 50a on holder 50 secures holder 50 to exhaust pipe 30 and provides a flow path via holder outlet 50b through which the heated air-fuel mixture is introduced as activated reductant into exhaust pipe 30. The activated reductant-exhaust gas mixture flows downstream to the NO_x abatement catalyst.

In an alternative embodiment of the present invention shown in Figure 6, exhaust treatment apparatus 20b comprises a mixer 26b that defines a mixing chamber therein and that accommodates an activating means comprising a miniature catalyst member 38 therein positioned to contact the fuel-oxygen mixture produced in mixer 26b. Mixer 26b may optionally comprise a modified fuel injector. Catalyst member 38 may be a plug-shaped member having a diameter of approximately 1 cm and a length of about 2.5 cm, and may be coated with a CPO catalytic material as described above. The catalyst member is positioned so that it can absorb sufficient heat from the exhaust gas in pipe 30 to attain a speciation temperature, even without a heat source, and so will facilitate speciation of the diesel fuel reductant into lower molecular weight hydrocarbon species prior to introducing the reductant into the exhaust gas stream. The embodiments of Figures 5A, 5B and Figure 6 provide mixing means for mixing oxygen and fuel and an activating means comprising either a heat source or a catalyst. In other embodiments, the activating means may optionally comprise both a heat source and a catalyst. For example, the heating element of glow plug 36 (Figure 5B) may be coated with a catalytic material effective to catalyze the partial oxidation (CPO) of the diesel fuel so that the glow plug heats both the CPO catalyst and the air-fuel mixture to a speciation temperature. The catalytic material, which may comprise, e.g., rhodium dispersed on alumina,

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may be coated onto the glow plug 36 in any conventional manner, but preferably, an anchor layer is deposited on the glow plug prior to application of the catalytic material. The anchor layer preferably comprises a nickel-aluminide material that is preferably thermally sprayed thereon in accordance with the teachings of U.S. patent application serial number 09/071,663, filed May 1, 1998, the disclosure of which is hereby incorporated herein by reference. Briefly restated, U.S. patent application 09/071,663 describes methods for applying anchor layers on various substrates. The disclosed methods, any of which may be employed to apply an anchor layer on the heating element of a glow plug, encompass thermal spraying processes in general, including plasma spraying, single wire plasma spraying, high velocity oxy-fuel spraying, combustion wire and/or powder spraying, electric arc spraying, etc. Electric arc spraying, e.g., twin wire arc spraying, of a metal (which term, as used herein and in the claims, includes mixtures of metals, including without limitation, metal alloys, pseudoalloys, and other intermetallic combinations) onto a metal or ceramic substrate was found to yield a structure having unexpectedly superior utility as a carrier for catalytic materials in the field of catalyst members. Twin wire arc spraying (encompassed herein by the term "wire arc spraying" and by the broader term "electric arc spraying") is a known process, as indicated by U.S. Patent 4,027,367 which is incorporated herein by reference. Briefly described, in the twin wire arc spray process, two feedstock wires act as two consumable electrodes. These wires are insulated from each other as they are fed to the spray nozzle of a spray gun in a fashion similar to wire flame guns. The wires meet in the center of a gas stream generated in the nozzle. An electric arc is initiated between the wires, and the current flowing through the wires causes their tips to melt. A compressed atomizing gas, usually air, is directed through the nozzle and across the arc zone, shearing off the molten droplets to form a spray that is propelled onto the substrate. Only metal wire feedstock can be used in an arc spray system because the feedstock must be conductive. The high particle temperatures created by the spray gun produce minute weld zones at the impact point on a metallic substrate. As a result, such electric arc spray coatings (sometimes referred to herein as "anchor layers") have good cohesive strength and a very good adhesive bond to the substrate.

The principal operating parameters in wire arc spraying include the voltage and amperage for the arc, the compression of the atomizing gas, the nozzle configuration and the stand-off from the substrate. The voltage is generally in the range of from 18 to 40 volts, and is typically in the range of from 28 to 32 volts; the current may be in the range of from about 100

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to 400 amps. The atomizing gas may be compressed to a pressure in the range of from about 30 to 70 psi. The nozzle configuration (e.g., slot aperture or cross aperture) and spray pattern vary in accordance with the desired nature of the anchor layer or may be chosen to accommodate the other parameters or the character of the substrate. A suitable stand-off is generally in the range of from about 4 to 10 inches from the substrate to the nozzle. Another operating parameter is the spray rate for the feedstock, a typical example of which would be 100 pounds per hour per 100 amps (4.5 kg/hr/100 amps). Still another parameter is the coverage or feedstock consumption rate, which may be, to give a particular example, 0.9 ounce per square foot per 0.001 inch thickness of the anchor layer. (It is typical to have a deposition efficiency of 70 percent (e.g., for spraying a plate) or less.)

Electric arc spray coatings are usually harder to finish (e.g., to grind down) and normally have higher spray rates than coatings of other thermal spray processes. Dissimilar electrode wires can be used to create an anchor layer containing a mixture of two or more different metal materials, referred to as a "pseudoalloy". Optionally, reactive gases can be used to atomize the molten feedstock to effect changes in the composition or properties of the applied anchor layer. On the other hand, it may be advantageous to employ an inert gas or at least a gas that does not contain oxygen or another oxidizing species. Oxygen, for example, may cause oxidation on the surface of a metal substrate or in the feedstock material and thus weaken the bond between the anchor layer and the substrate.

Anchor layers of a variety of compositions can be deposited on a substrate in accordance with the present invention by utilizing, without limitation, feedstocks of the following metals and metal mixtures: Ni, Ni/Al, Ni/Cr, Ni/Cr/Al/Y, Co/Cr, Co/Cr/Al/Y, Co/Ni/Cr/Al/Y, Fe/Al, Fe/Cr, Fe/Cr/Al, Fe/Cr/Al/Y, Fe/Ni/Al, Fe/Ni/Cr, 300 and 400 series stainless steels, and, optionally, mixtures of one or more thereof. One specific example of a metal useful for wire arc spraying onto a substrate in accordance with the present invention is a nickel/aluminum alloy that generally contains at least about 90% nickel and from about 3% to 10% aluminum, preferably from about 4% to 6% aluminum by weight. Such an alloy may contain minor proportions of other metals referred to herein as "impurities" totaling not more than about 2% of the alloy. A preferred specific feedstock alloy comprises about 95% nickel and 5% aluminum and may have a melting point of about 2642°F. Some such impurities may be included in the alloy for various purposes, e.g., as processing aids to facilitate the wire arc spraying process or the formation of the anchor layer, or to provide the anchor layer with favorable properties.

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It has also been found that electric arc spraying a metal onto a metal substrate yields an unexpectedly superior carrier for catalytic materials relative to carriers having metal anchor layers applied thereto by other methods. Catalytic materials have been seen to adhere better to a carrier comprising an electric arc sprayed anchor layers than to a carrier comprising a substrate without an intermediate layer applied thereto and even better than to a carrier comprising a substrate having a metal layer deposited thereon by plasma spraying. Absent an electric arc sprayed anchor layer, catalytic materials disposed on metal substrates, with or without intermediate layers between the substrate and the catalytic material, often did not adhere sufficiently well to the substrate to provide a commercially acceptable product. For example, a metal substrate having a metal intermediate layer that was plasma-sprayed thereon and having a catalytic material applied to the intermediate layer failed to retain the catalytic material, which flaked off upon routine handling, apparently due to a failure of the intermediate layer to bond with the substrate. The catalytic material on other carriers was seen to spall off upon normal use, apparently as a result of being subjected to a high gas flow rate, to thermal cycling, to the eroding contact of high temperature steam and other components of the exhaust gas stream, vibrations, etc. Electric arc spraying has therefore been found to improve the durability of catalyst members comprising catalytic materials carried on carrier substrates by improving their durability.

Surprisingly, it was found that electric arc spraying, of which wire arc spraying is a particular embodiment, of a metal onto a metal substrate results in a superior bond between the resulting anchor layer and the substrate relative to plasma spraying. An electric arc sprayed anchor layer is believed to have at least two characteristics that distinguish it from anchor layers applied by plasma spraying: a superior anchor layer-metallic substrate interface bond and a highly irregular or "rough" surface. It is believed that the anchor layer-metallic substrate interface bond may be the result of diffusion between the sprayed material and the metallic substrate that is achieved at their interface despite the relatively low temperature at which wire arc spraying is practiced. For example, the electric arc temperature may be not more than 10,000°F. In such case, the temperature of the molten feedstock is expected to be at a temperature of not more than about 5000°F, preferably in the range of 1000° to 4000° F, more preferably not more than about 2000°F. The low temperature is also believed to be responsible for the especially uneven surface of the anchor layer because the sprayed material cools on the substrate (whether metal or ceramic) to its freezing temperature so quickly that it does not flow

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significantly on the substrate surface and therefore does not smooth out. Instead, it freezes into an irregular surface configuration. Accordingly, the surface of the anchor layer has a rough profile that provides a superior physical anchor for catalytic components and materials disposed thereon. The rough profile appears to be the result of "pillaring", the formation of small, pillar-like structures resulting from the sequential deposition and freezing of one molten drop of feedstock material atop another.

It does not appear to be important to match the sprayed metal to the metal of the substrate, i.e., to the metal of the heating element of the glow plug. While the catalytic material and the optional anchor layer tend to insulate the glow plug and to interfere with heat transfer therefrom, a catalyzed glow plug does nevertheless provide a means for the catalytic partial oxidation of the diesel fuel.

The exhaust treatment apparatus 20c shown in Figure 7A comprises an mixing means comprising a conventional fuel injector 26c that receives air and fuel via lines 18' and 34 as described above and injects an unactivated mixture thereof into exhaust pipe 30. To facilitate activation, the fuel-air mixture is isolated from the exhaust gas within exhaust pipe 30 by a reductant conduit 40. The exhaust gases contacting conduit 40 may be sufficiently hot to create activating conditions within conduit 40 without an added heat source so that the reductant emitted at outlet 40a for mixture with the exhaust gas is activated for the reduction of NO_x at NO_x abatement catalyst 22. However, exhaust pipe 30 and conduit 40 may be adapted to accommodate a heat source structure that serves to create activating conditions therein. For example, Figure 7A shows a glow plug 36 for heating the air-fuel mixture and a CPO catalyst member 38a which are mounted in exhaust pipe 30 and conduit 40 for contact with the mixture. In addition, catalyst member 38a is surrounded by an electric heating element 42 comprising heating coils that serve to raise catalyst member 38a to its working (i.e., speciating) temperature. It will be understood that it is not necessary to use all the illustrated activating structures shown in Figure 7A, but rather that each may be used singly or they may be used in various combinations.

Another specific embodiment of the present invention is shown schematically in Figure 7B. In Figure 7B, activated reductant means 220 comprises a mixer comprising a fuel injector 126d that has a fuel inlet 126e, an air inlet 126f and an outlet 126g for emitting an air-fuel mixture produced therein. There is also a heating means comprising an electric heating element 142 connected to the injector outlet 126g. Heating element 142 defines an interior chamber

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within which a catalyst member 138 comprising a carrier core measuring 1 inch in length and 0.4 inch diameter that is coated with a CPO catalytic material. The catalyst member is mounted in heating element 142 with a gasket seal 138a. Heating element 142 has an outlet which is connected to and provides flow communication with exhaust pipe 30. In use, fuel and air are introduced into injector 126 and an air-fuel mixture is released therefrom into heating element 142. The air-fuel reductant mixture flows through catalyst member 138. The air-fuel mixture and the CPO catalyst are heated by heating element 142 to a temperature at which speciation occurs, to activate the reductant. The activated reductant flows through a heating unit outlet 142a into exhaust pipe 30 where it is mixed with the exhaust gases and from where it flows downstream to the NO_x abatement catalyst.

Although the present invention has been described in detail with respect to specific preferred embodiments thereof, it will be appreciated that various modifications thereto lie within the spirit and scope of the appended claims.

THE CLAIMS

What is claimed is:

5 1. An apparatus effective for generating activated reductant, comprising:
a mixer for receiving and mixing a source hydrocarbon and oxygen; and
activation means for speciating the source hydrocarbon to produce activated
reductant.

10 2. An apparatus for generating activated hydrocarbon species from source
hydrocarbons, comprising:
a mixer having inlets for receiving the source hydrocarbon and oxygen, a mixing
chamber for creating a mixture of the source hydrocarbon and oxygen and an outlet for
discharging activated hydrocarbon species; and
15 a catalyst disposed for contact with the mixture, the catalyst being effective for
activating the source hydrocarbon.

3. The apparatus of claim 2 wherein the catalyst is disposed in the mixer.

20 4. The apparatus of claim 3 comprising a glow plug comprising a catalyzed heating
element disposed in the mixer.

5. An apparatus for generating activated hydrocarbon species from source
hydrocarbons, comprising:

25 a mixer having inlets for receiving the source hydrocarbon and oxygen, a mixing
chamber for creating a mixture of the source hydrocarbon and oxygen and an outlet for
discharging activated hydrocarbon species; and

a heating element positioned to generate activated hydrocarbons from the mixture of
the source hydrocarbon and oxygen.

30

6. The apparatus of claim 5 wherein the heating element is disposed in the mixer.

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7. The apparatus of claim 6 comprising a glow plug mounted thereon with the heating element in the mixer.

8. The apparatus of claim 5 wherein the heating element is positioned to contact the mixture discharged from the outlet of the mixer to generate activated hydrocarbon species therefrom.

9. The apparatus of claim 8 wherein the heating element has a heater inlet connected to the mixer outlet for receiving the mixture of source hydrocarbon and oxygen and a heater outlet for discharging activated hydrocarbon species.

10. The apparatus of claim 9 further comprising a catalyst in the heating element positioned to contact the mixture prior to discharge of the activated hydrocarbon species from the heater outlet.

15

11. The apparatus of any one of claims 1 through 10 further comprising a temperature sensor for sensing the temperature of a gas stream and at least one oxygen sensor for sensing whether such gas stream is lean, and further comprising a control unit responsive to the sensors, for initiating the apparatus when the oxygen sensor indicates a lean gas stream and the temperature sensor indicates a temperature of less than 200°C.

20

12. The apparatus of claim 11 wherein the control unit is configured to initiate the apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C.

25

13. The apparatus of claim 1 or claim 2 further comprising an air pump connected for delivering oxygen to the mixer and a fuel pump connected for delivering source hydrocarbon to the mixer.

30

14. The apparatus of claim 13 further comprising a temperature sensor for sensing the temperature of a gas stream and an oxygen sensor for sensing whether the gas stream is lean, and further comprising a control unit responsive to the sensors, for initiating the apparatus when

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the oxygen sensor indicates a lean gas stream and the temperature sensor indicates a temperature of less than 200°C, wherein activating the apparatus comprises activating the air pump and the fuel pump.

5 15. The apparatus of claim 14 wherein the control unit is configured to initiate the apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C.

10 16. The apparatus of any one of claims 2 through 10 further comprising an air pump connected to a mixer inlet for delivering oxygen to the mixer and a fuel pump connected to a mixer inlet for delivering source hydrocarbon to the mixer.

15 17. The apparatus of claim 16 further comprising a temperature sensor for sensing the temperature of a gas stream and an oxygen sensor for sensing whether the gas stream is lean, and further comprising a control unit responsive to the sensors, for initiating the apparatus when the oxygen sensor indicates a lean gas stream and the temperature sensor indicates a temperature of less than 200°C, wherein activating the apparatus comprises activating the air pump and the fuel pump.

20 18. The apparatus of claim 17 wherein the control unit is configured to initiate the apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C.

25 19. An apparatus effective at least for the reduction of oxides of nitrogen (NO_x) in a gas stream, the apparatus comprising:

 a supply of source hydrocarbon;

 a source of oxygen;

 a mixer for receiving source hydrocarbon from the supply and for receiving the oxygen and for producing a mixture thereof;

30 activation means for speciating the source hydrocarbon in the mixture to produce activated reductant and providing the activated reductant to the gas stream; and

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a NO_x-reduction catalyst positioned for contact with the gas stream with the activated reductant therein.

20. The apparatus of claim 19 wherein the activation means comprises a glow plug
5 comprising a catalyzed heating element disposed in the mixing chamber.

21. An apparatus effective at least for the reduction of oxides of nitrogen (NO_x) in a gas stream, the apparatus comprising:

a supply of source hydrocarbon;

10 a source of oxygen;

a mixer having inlets for receiving the source hydrocarbon and oxygen, a mixing chamber for creating a mixture of the source hydrocarbon and oxygen and an outlet for discharging activated hydrocarbon species to the gas stream;

a catalyst in the mixing chamber effective for activating the source hydrocarbon;

15 and

a NO_x-reduction catalyst positioned for contact with the gas stream and the activated reductant therein.

22. The apparatus of claim 21 wherein the source hydrocarbon comprises diesel fuel.
20

23. An apparatus effective at least for the reduction of oxides of nitrogen (NO_x) in a gas stream, the apparatus comprising:

a mixer having inlets for receiving the source hydrocarbon and oxygen, a mixing chamber for creating a mixture of the source hydrocarbon and oxygen and having an outlet for
25 discharging activated hydrocarbon species to the gas stream; and

a heating element positioned to generate activated hydrocarbons from the mixture of the source hydrocarbon and oxygen; and

a NO_x-reduction catalyst positioned for contact with the gas stream and the activated reductant therein.
30

24. The apparatus of claim 23 wherein the heating element is disposed in the mixer.

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25. The apparatus of claim 24 comprising a glow plug mounted thereon with the heating element in the mixer.

26. The apparatus of claim 24 wherein the heating element is positioned to contact the mixture discharged from the outlet of the mixer to generate activated hydrocarbon species therefrom.

27. The apparatus of claim 26 wherein the heating element has a heater inlet connected to the mixer outlet for receiving the mixture of source hydrocarbon and oxygen and a heater outlet for discharging activated hydrocarbon species.

28. The apparatus of claim 27 comprising a catalyst in the heating element positioned to contact the mixture prior to discharge of the activated hydrocarbon species from the heater outlet.

15

29. The apparatus of any one of claims 19-28 further comprising a temperature sensor for sensing the temperature of a gas stream and an oxygen sensor for sensing whether such gas stream is lean, and further comprising a control unit responsive to the sensors, for initiating the apparatus when the oxygen sensor indicates a lean gas stream and the temperature sensor indicates a temperature of less than 200°C.

20

30. The apparatus of claim 29 wherein the control unit is configured to initiate the apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C.

25

31. The apparatus of claim 19 further comprising an air pump connected for delivering oxygen to the mixer and a fuel pump connected for delivering source hydrocarbon to the mixer.

32. The apparatus of claim 31 further comprising a temperature sensor for sensing the temperature of the gas stream contacting the NO_x-reduction catalyst and an oxygen sensor for sensing whether the gas stream is lean, and further comprising a control unit responsive to the sensors, for initiating the apparatus when the oxygen sensor indicates a lean gas stream and the

30

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temperature sensor indicates a temperature of less than 200°C, wherein activating the apparatus comprises activating the air pump and the fuel pump.

33. The apparatus of claim 32 wherein the control unit is configured to initiate the
5 apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C.

34. The apparatus of any of claims 19 through 28 further comprising an air pump
connected to a mixer inlet for delivering oxygen to the mixer and a fuel pump connected to a
10 mixer inlet for delivering source hydrocarbon to the mixer.

35. The apparatus of claim 34 further comprising a temperature sensor for sensing the
temperature of the gas stream contacting the NO_x-reduction catalyst and an oxygen sensor for
sensing whether the gas stream is lean, and further comprising a control unit responsive to the
15 sensors, for initiating the apparatus when the oxygen sensor indicates a lean gas stream and the
temperature sensor indicates a temperature of less than 200°C, wherein activating the apparatus
comprises activating the air pump and the fuel pump.

36. The apparatus of claim 35 wherein the control unit is configured to initiate the
20 apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C.

37. A method for producing an activated hydrocarbon species, comprising mixing a
source hydrocarbon with oxygen and subjecting the mixture to activating conditions.
25

38. The method of claim 37 wherein the source hydrocarbon comprises diesel fuel.

39. The method of claim 37 or claim 38 comprising contacting the mixture with a
catalytic material effective to facilitate speciation of the source hydrocarbon.
30

40. The method of claim 37 or claim 38 comprising heating the mixture to a
temperature of at least about 350°C.

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41. The method of claim 39 comprising contacting the mixture at a temperature lower than 350°C with a catalyst effective to facilitate speciation at such lower temperature.

42. The method of claim 41 comprising contacting the mixture with the catalyst at a
5 temperature in the range of from about 200°C to 340°C.

43. An activated hydrocarbon reductant produced by a method comprising mixing a source hydrocarbon with oxygen and subjecting the mixture to activating conditions.

10 44. The activated hydrocarbon species produced by the method of claim 37 wherein the source hydrocarbon comprises diesel fuel.

45. The activated hydrocarbon species produced by the method of claim 37 or claim 38 wherein the method further comprises contacting the mixture with a catalytic material effective
15 to facilitate speciation of the source hydrocarbon.

46. The activated hydrocarbon species produced by the method of claim 37 or claim 38 further comprising heating the mixture to a temperature of at least about 350°C.

20 47. The activated hydrocarbon species produced by the method of claim 39 and further comprising contacting the mixture at a temperature lower than 350°C with a catalyst effective to facilitate speciation at such lower temperature.

48. The activated hydrocarbon species produced by the method of claim 42 and further
25 comprising contacting the mixture with the catalyst at a temperature in the range of from about 200°C to 340°C.

49. A method for reducing oxides of nitrogen (NO_x) in a lean gas stream, comprising:
creating a fuel-oxygen mixture by mixing diesel fuel vapor with oxygen, subjecting
30 the fuel-oxygen mixture to activating conditions to create an activated diesel reductant;
mixing the activated diesel reductant into the gas stream; and

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contacting the gas stream with the activated diesel reductant therein with a NO_x-reduction catalyst.

50. The method of claim 49 comprising heating the fuel-oxygen mixture to about 350°C
5 before adding the fuel-oxygen mixture to the gas stream.

51. The method of claim 49 comprising contacting the fuel-oxygen mixture with a catalytic material.

10 52. The method of claim 49, claim 50 or claim 51 comprising mixing the activated diesel reductant with the gas stream at a temperature below 200°C.

53. The method of claim 52 comprising mixing the activated diesel reductant with the gas stream at a temperature in the range of about 140°C to 200°C.

15

54. The method of claim 53 comprising mixing the activated diesel reductant with the gas stream at a temperature in the range of about 140°C to 160°C.

55. A method of operating an apparatus for the reduction of NO_x in a lean gas stream,
20 comprising:

flowing the gas stream into contact with a NO_x-reduction catalyst;

sensing the temperature of the gas stream contacting the NO_x-reduction catalyst; and

introducing activated diesel reductant into the gas stream for contact with the NO_x-reduction catalyst when the temperature of the gas stream is in the range of 140°C to 200°C.

25

56. The method of claim 55 comprising introducing the activated diesel reductant into the gas stream when the temperature of the gas stream is in the range of 140°C to 160°C.

57. A method for operating an apparatus effective at least for the reduction of oxides of
30 nitrogen (NO_x) in a gas stream, the apparatus comprising a supply of source hydrocarbon, a source of oxygen, activated reductant means for mixing the source hydrocarbon and oxygen, speciating the source hydrocarbon to produce activated reductant and providing the activated

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reductant to the gas stream, and a NO_x-reduction catalyst positioned for contact with the gas stream with the activated reductant therein, the method comprising operating the activated reductant means, the supply of source hydrocarbon, and the source of oxygen when the gas stream is lean and when the temperature of the gas stream contacting the NO_x-reduction catalyst is at a temperature less than 200°C.

58. The method of claim 57 comprising operating the activated reductant means when the temperature of the exhaust gas is in the range of about 140°C to 160°C.

10 59. In a glow plug comprising a heating element extending from a plug body, the improvement comprising that a coating of catalytic material is carried on the heating element, the catalytic material being effective to facilitate the speciation of a source hydrocarbon.

60. The glow plug of claim 59 wherein the improvement further comprises an anchor layer on the heating element between the heating element and the catalytic material.

61. The glow plug of claim 60 wherein the improvement further comprises that the anchor layer comprises a metal that is thermally sprayed onto the heating element of the glow plug.

20 62. The glow plug of claim 61 wherein the improvement further comprises that the anchor layer is electric arc sprayed onto the heating element of the glow plug.

63. The glow plug of claim 61 wherein the improvement further comprises that the anchor layer is deposited by electric arc spraying a metal feedstock selected from the group consisting of nickel, Ni/Al, Ni/Cr, Ni/Cr/Al/Y, Co/Cr, Co/Cr/Al/Y, Co/Ni/Cr/Al/Y, Fe/Al, Fe/Cr, Fe/Cr/Al, Fe/Cr/Al/Y, Fe/Ni/Al, Fe/Ni/Cr, 300 series stainless steels, 400 series stainless steels, and mixtures of two or more thereof.

30 64. The glow plug of claim 63 wherein the improvement further comprises that the anchor layer comprises nickel and aluminum.

65. The glow plug of claim 64 wherein the improvement comprises that the aluminum comprises from about 3 to 10 percent of the combined weights of nickel and aluminum in the anchor layer.

5 66. The glow plug of claim 64 wherein the improvement comprises that the aluminum comprises from about 4 to 6 percent of the combined weights of nickel and aluminum in the anchor layer.

10 67. The glow plug of claim 59 wherein the improvement comprises that the catalytic material is deposited on the anchor layer and comprises a refractory metal oxide support on which one or more catalytic metal components are dispersed.

AMENDED CLAIMS

[received by the International Bureau on 11 May 2001 (11.05.01);
original claims 1-67 replaced by new claims 1-73 (8 pages)]

5 1. Canceled.

 2. Canceled.

 3. Canceled.

10

 4. Canceled.

 5. An apparatus for generating activated reductant from source hydrocarbons without the use of a catalyst member, the apparatus consisting essentially of:

15 a mixer having inlets for receiving the source hydrocarbon and oxygen, a mixing chamber for creating a mixture of the source hydrocarbon and oxygen and an outlet for discharging activated hydrocarbon species; and

 a heating element capable of heating the mixture to at least about 350°C to generate activated hydrocarbons therefrom.

20

 6. The apparatus of claim 5 wherein the heating element is disposed in the mixer.

 7. The apparatus of claim 6 comprising a glow plug mounted thereon with the heating element in the mixer.

25

 8. The apparatus of claim 5 wherein the heating element is positioned to contact the mixture discharged from the outlet of the mixer to generate activated hydrocarbon species therefrom.

30

 9. The apparatus of claim 8 wherein the heating element has a heater inlet connected to the mixer outlet for receiving the mixture of source hydrocarbon and oxygen and a heater outlet for discharging activated hydrocarbon species.

10. Canceled.

11. The apparatus of any one of claims 5 through 9 further comprising a temperature sensor for sensing the temperature of a gas stream and at least one oxygen sensor for sensing whether such gas stream is lean, and further comprising a control unit responsive to the sensors, the control unit operating the apparatus when the oxygen sensor indicates a lean gas stream and the temperature sensor indicates a temperature of less than about 200°C.

12. The apparatus of claim 11 wherein the control unit is configured to operate the apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C.

13. Canceled.

14. Canceled.

15. Canceled.

16. The apparatus of any one of claims 5 through 9 further comprising an air pump connected to a mixer inlet for delivering oxygen to the mixer and a fuel pump connected to a mixer inlet for delivering source hydrocarbon to the mixer.

17. The apparatus of claim 16 further comprising a temperature sensor for sensing the temperature of a gas stream and an oxygen sensor for sensing whether the gas stream is lean, and further comprising a control unit responsive to the sensors, the control unit operating the apparatus when the oxygen sensor indicates a lean gas stream and the temperature sensor indicates a temperature of less than 200°C, wherein operating the apparatus comprises operating the air pump and the fuel pump.

18. The apparatus of claim 17 wherein the control unit is configured to operate the apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C.

19. Canceled.

20. Canceled.

21. An apparatus effective at least for the reduction of oxides of nitrogen (NO_x) in a gas stream, the apparatus comprising:

5 a supply of source hydrocarbon;

a source of oxygen;

a mixer having inlets for receiving the source hydrocarbon and oxygen, a mixing chamber for creating a mixture of the source hydrocarbon and oxygen in amounts that provide a $\text{O}_2:\text{C}$ ratio in the range of from about 0.3:1 to 0.8:1 and having an outlet to the gas stream;

10 a catalyst comprising a platinum group metal effective for the catalytic partial oxidation of the source hydrocarbon to produce activated reductant therefrom; and

a NO_x -reduction catalyst positioned for contact with the gas stream and the activated reductant therein.

15 22. Canceled.

23. An apparatus effective at least for the reduction of oxides of nitrogen (NO_x) in a gas stream, the apparatus comprising:

20 a mixer having inlets for receiving the source hydrocarbon and oxygen, a mixing chamber for creating a mixture of the source hydrocarbon and oxygen and having an outlet for discharging activated hydrocarbon species to the gas stream; and

a non-catalyzed heating element positioned to generate activated hydrocarbons from the mixture of the source hydrocarbon and oxygen; and

25 a NO_x -reduction catalyst positioned for contact with the gas stream and the activated reductant therein.

24. The apparatus of claim 23 wherein the heating element is disposed in the mixer.

30 25. The apparatus of claim 24 comprising a glow plug mounted thereon with the heating element in the mixer.

26. The apparatus of claim 24 wherein the heating element is positioned to contact the mixture discharged from the outlet of the mixer to generate activated hydrocarbon species therefrom.

5 27. The apparatus of claim 26 wherein the heating element has a heater inlet connected to the mixer outlet for receiving the mixture of source hydrocarbon and oxygen and a heater outlet for discharging activated hydrocarbon species.

28. Canceled.

10 29. The apparatus of any one of claims 21 or 23 through 27 further comprising a temperature sensor for sensing the temperature of a gas stream and an oxygen sensor for sensing whether such gas stream is lean, and further comprising a control unit responsive to the sensors, for operating the apparatus when the oxygen sensor indicates a lean gas stream and the
15 temperature sensor indicates a temperature of less than about 200°C.

30. The apparatus of claim 29 wherein the control unit is configured to operate the apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C.

20 31. Canceled.

32. Canceled.

25 33. Canceled.

34. The apparatus of any of claims 21 or 23 through 27 further comprising an air pump connected to a mixer inlet for delivering oxygen to the mixer and a fuel pump connected to a mixer inlet for delivering source hydrocarbon to the mixer.

30 35. The apparatus of claim 34 further comprising a temperature sensor for sensing the temperature of the gas stream contacting the NO_x-reduction catalyst and an oxygen sensor for sensing whether the gas stream is lean, and further comprising a control unit responsive to the sensors, for operating the apparatus when the oxygen sensor indicates a lean gas stream and the

temperature sensor indicates a temperature of less than 200°C, wherein operating the apparatus comprises operating the air pump and the fuel pump.

36. The apparatus of claim 35 wherein the control unit is configured to operate the
5 apparatus when the temperature sensor indicates a temperature in the range of about 140°C to 160°C.

37. Canceled.

10 38. Canceled.

39. Canceled.

15 40. Canceled.

41. Canceled.

42. Canceled.

20 43. An activated hydrocarbon reductant produced by a method comprising mixing a source hydrocarbon with oxygen in quantities which provide a O₂:C ratio in the range of from about 0.3:1 to 0.8:1, and heating the mixture to a temperature of at least about 350°C in the absence of a catalyst.

25 44. The activated hydrocarbon species produced by the method of claim 43 wherein the source hydrocarbon comprises diesel fuel.

45. Canceled.

30 46. Canceled.

47. Canceled.

48. Canceled.

49. A method for reducing oxides of nitrogen (NO_x) in a lean gas stream, comprising:
adding activated reductant to the gas stream when the gas stream is at a temperature
below about 200°C ; and

contacting the gas stream with the activated reductant therein with a NO_x -reduction
5 catalyst.

50. The method of claim 49 comprising generating the activated reductant by mixing a
source hydrocarbon with oxygen and in proportions that provide a $\text{O}_2:\text{C}$ ratio in the range of
from about 0.3 to 0.8:1 and heating the mixture to about 350°C to produce the activated
10 reductant without the use of a catalyst.

51. The method of claim 49 comprising generating the activated reductant by mixing a
source hydrocarbon with oxygen and in proportions that provide a $\text{O}_2:\text{C}$ ratio in the range of
from about 0.3 to 0.8:1 and contacting the mixture with a catalyst comprising a platinum group
15 metal effective to catalyze the catalytic partial oxidation of the source hydrocarbon to produce
the activated reductant.

52. Canceled.

20 53. The method of claim 49, 50 or 51 comprising mixing the activated reductant with
the gas stream at a temperature in the range of from about 140°C to 200°C .

54. The method of claim 53 comprising mixing the activated diesel reductant with the
gas stream at a temperature in the range of about 140°C to 160°C .

25

55. Canceled.

56. Canceled.

30 57. Canceled.

58. Canceled.

59. Canceled.

35

60. Canceled.

61. Canceled.

5 62. Canceled.

63. Canceled.

64. Canceled.

10

65. Canceled.

66. Canceled.

15 67. Canceled.

68. An apparatus effective at least for the reduction of oxides of nitrogen (NO_x) in a gas stream, the apparatus comprising:

a supply of source hydrocarbon;

20 a source of oxygen;

a mixer for receiving source hydrocarbon from the supply and for receiving the oxygen and for producing a mixture thereof;

a catalyst comprising a platinum group metal effective for the catalytic partial oxidation of the source hydrocarbon in the mixture to produce activated reductant therefrom;

25 a NO_x -reduction catalyst member positioned for contact with the gas stream with the activated reductant therein;

a temperature sensor for sensing the temperature of a gas stream;

at least one oxygen sensor for sensing whether such gas stream is lean; and

30 a control unit responsive to the sensors, for operating the apparatus to produce activated reductant when the oxygen sensor indicates a lean gas stream and the temperature sensor indicates a temperature of less than about 200°C .

69. The apparatus of claim 68 wherein the control unit is configured to initiate the apparatus when the temperature sensor indicates a temperature in the range of from about 140°C to 160°C.

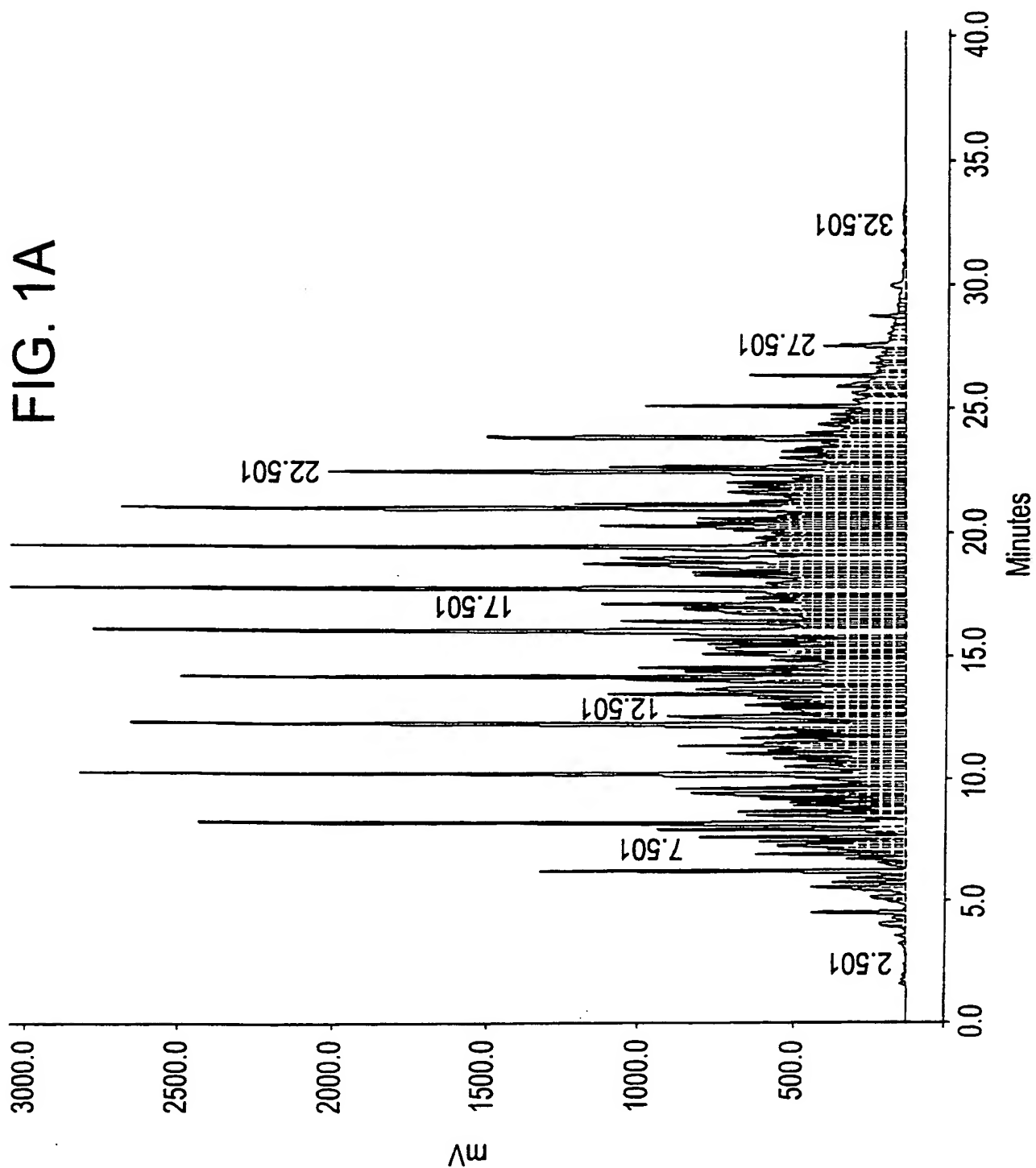
5 70. A method for producing an activated hydrocarbon species, comprising mixing a source hydrocarbon with oxygen and contacting with a non-catalyzed heating element at a temperature of at least about 350°C.

10 71. The method of claim 70 comprising providing the source hydrocarbon and oxygen in quantities sufficient to provide a O₂:C ratio in the range of from about 0.3:1 to 0.8:1.

 72. The method of claim 70 or claim 71 wherein the source hydrocarbon comprises diesel fuel.

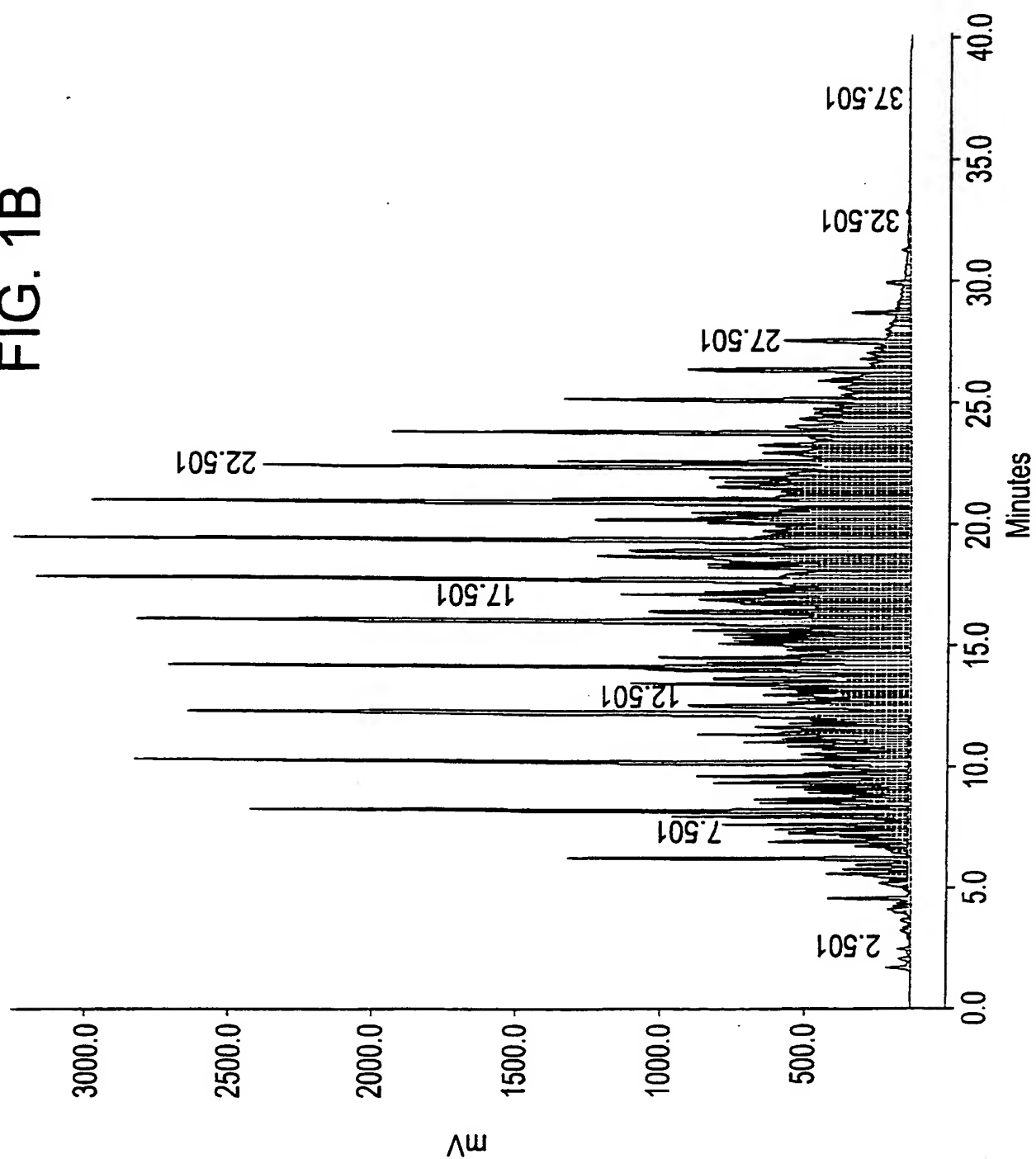
15 73. The method of any one of claims 49, 50 or 51 comprising generating the activated reductant from diesel fuel and oxygen.

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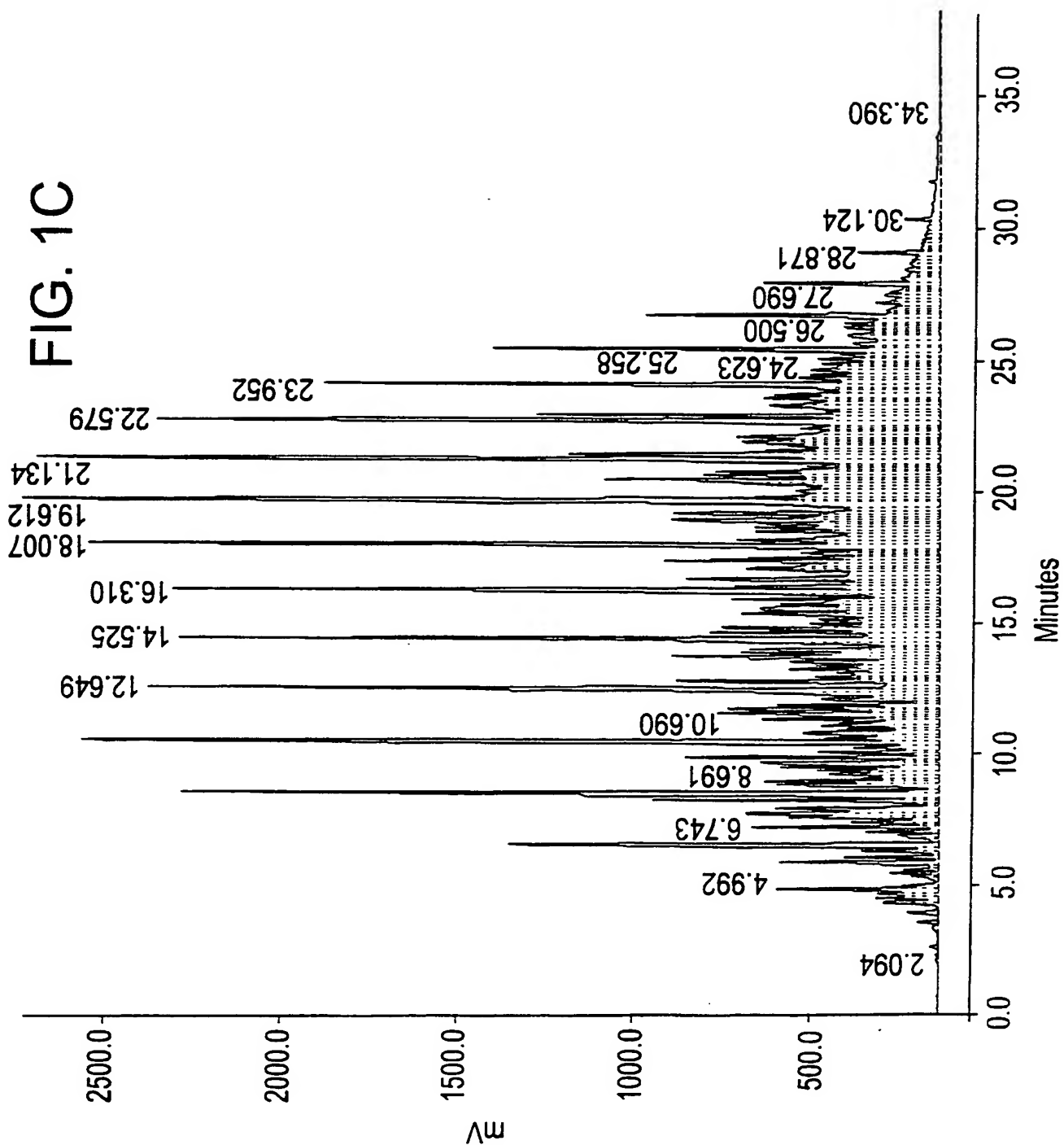


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FIG. 1B

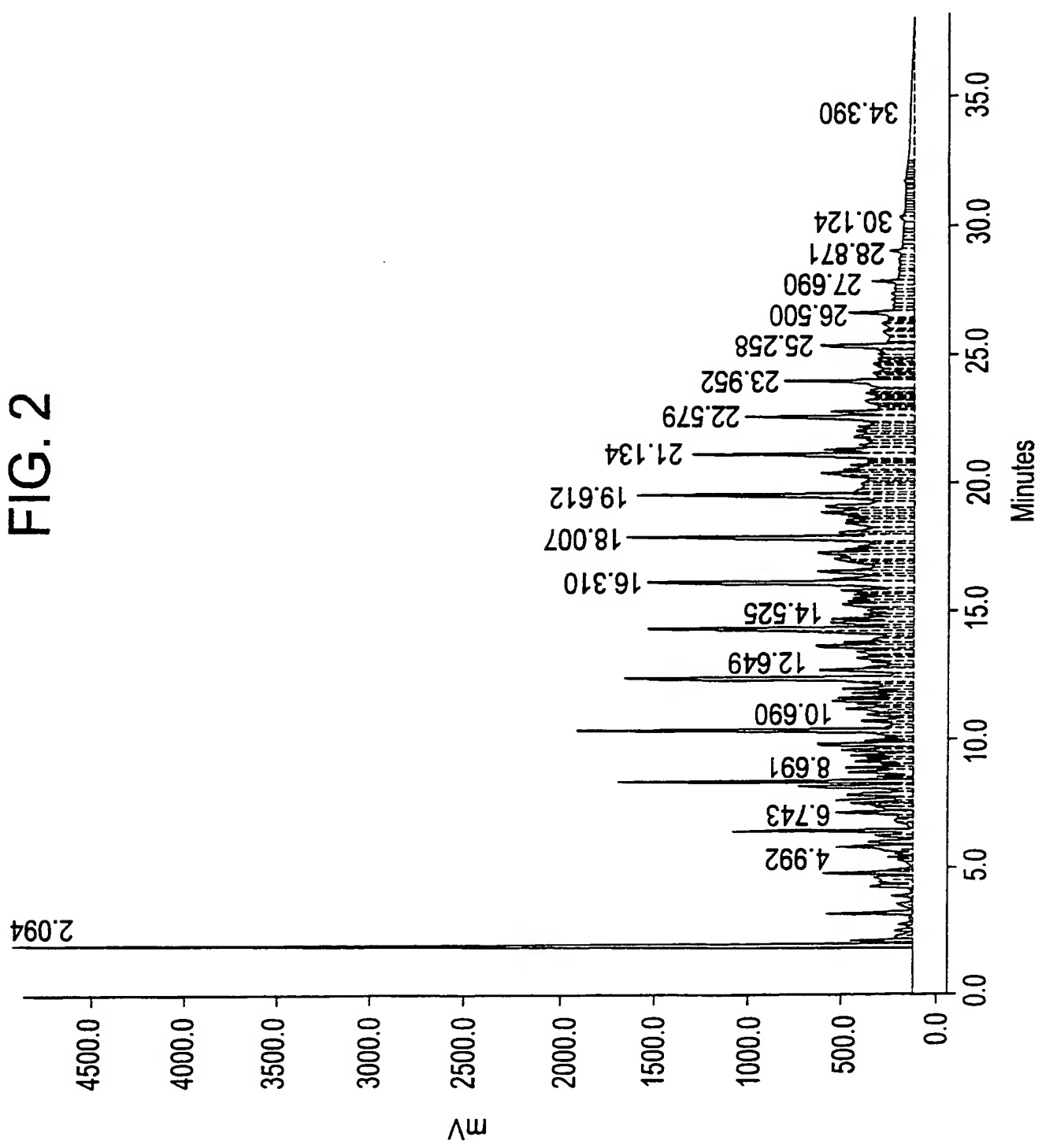


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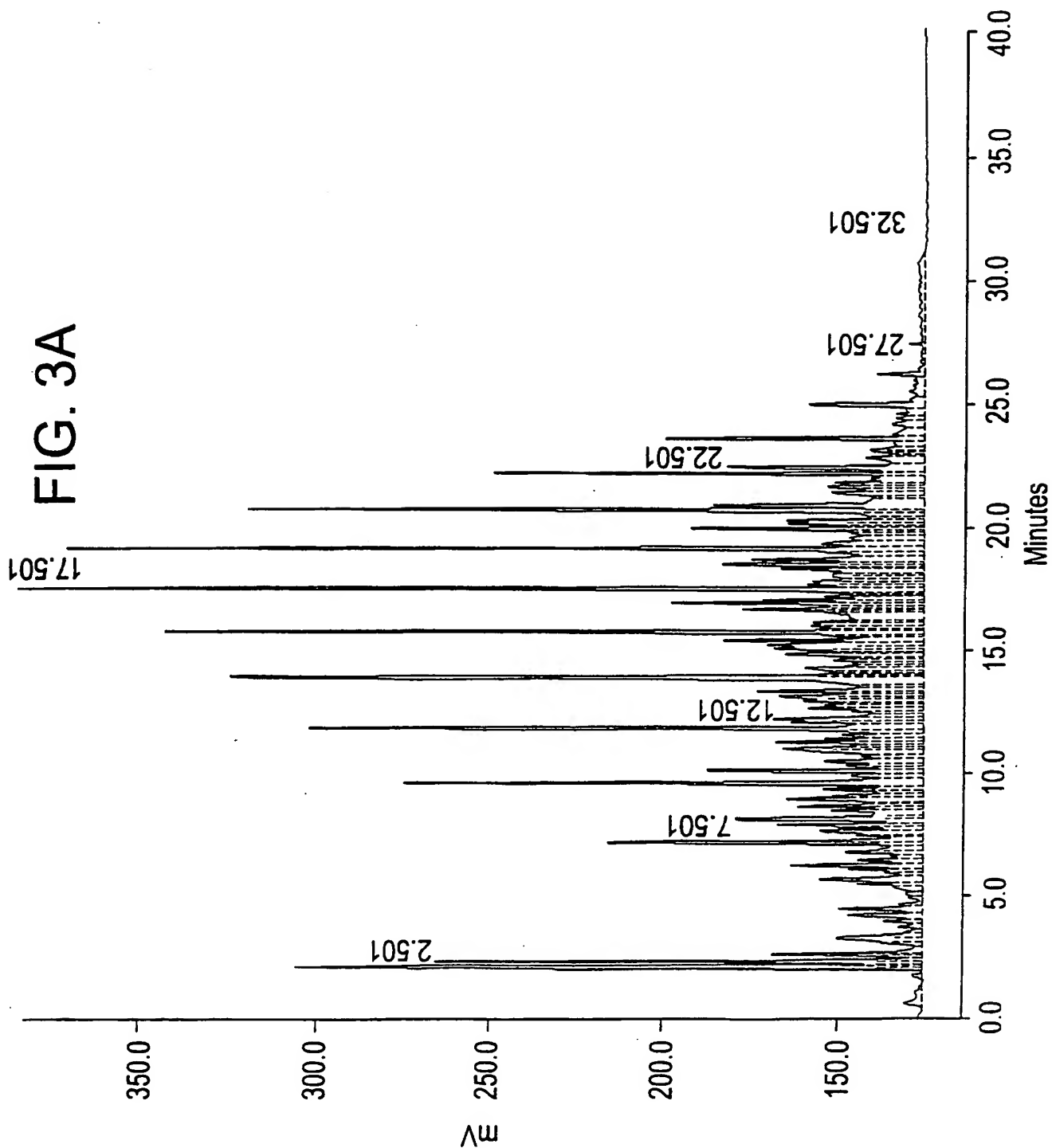


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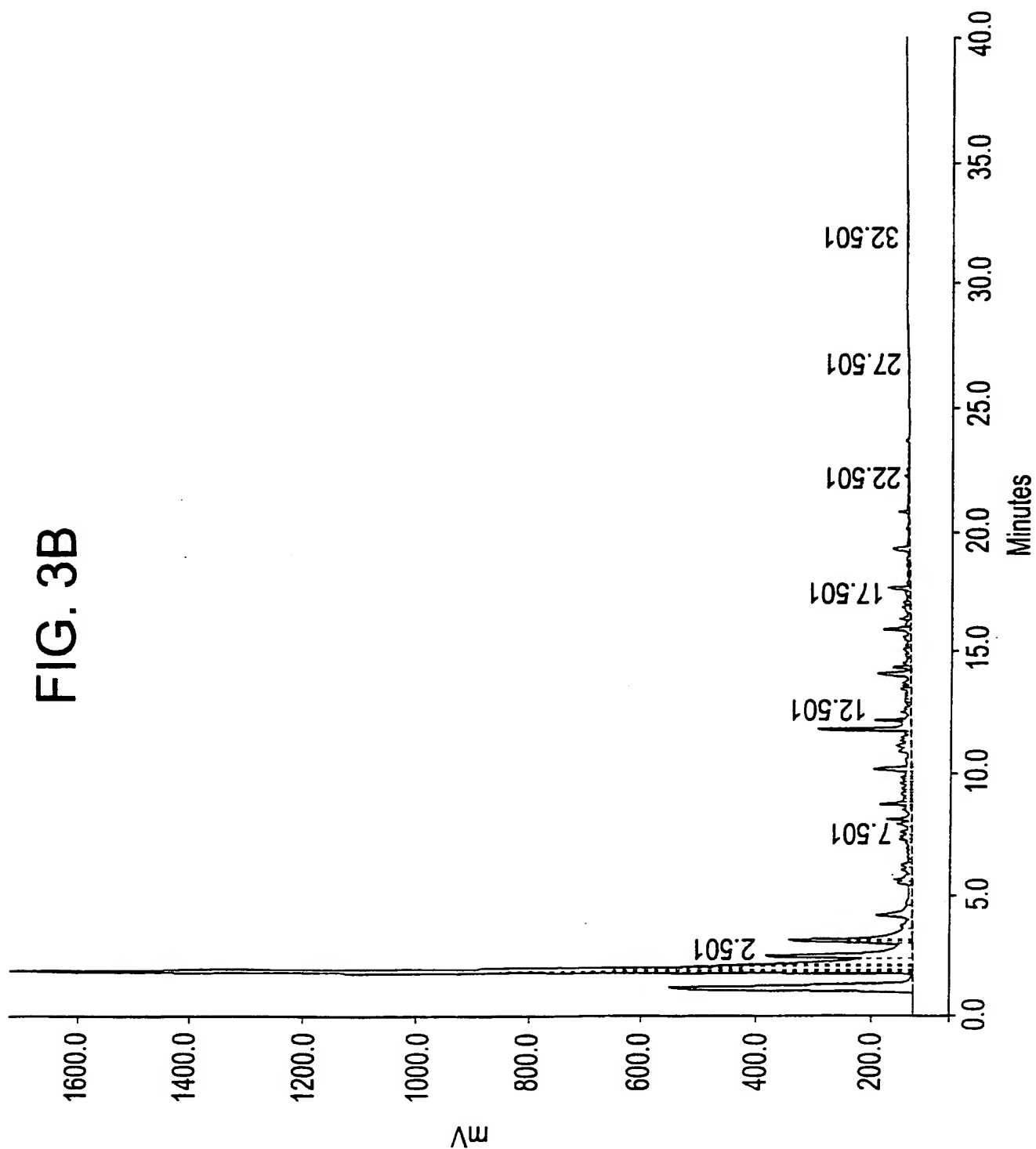
FIG. 2



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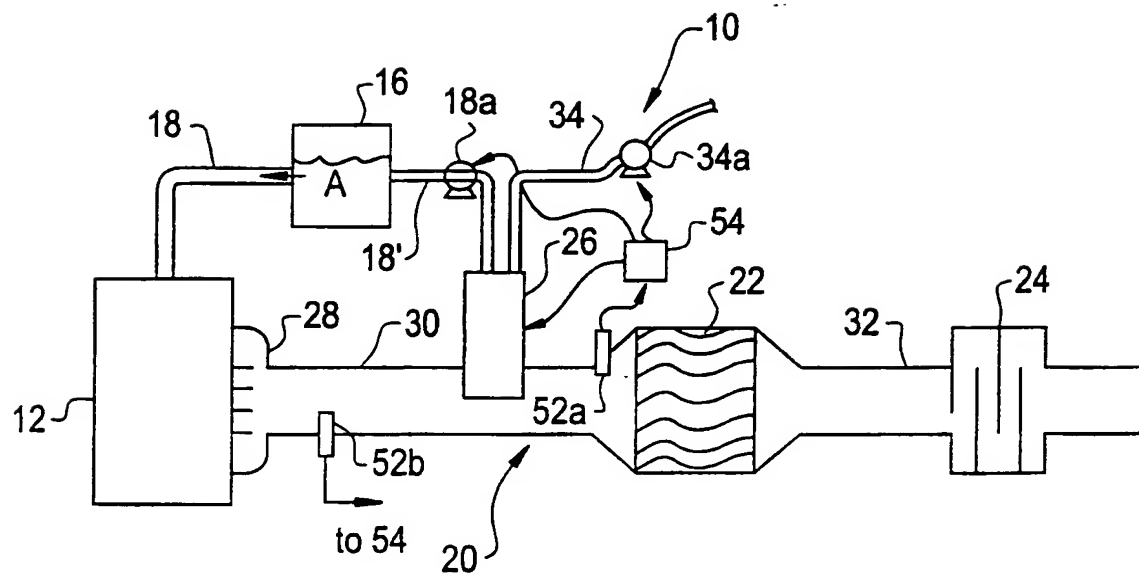


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FIG. 4



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FIG. 5A

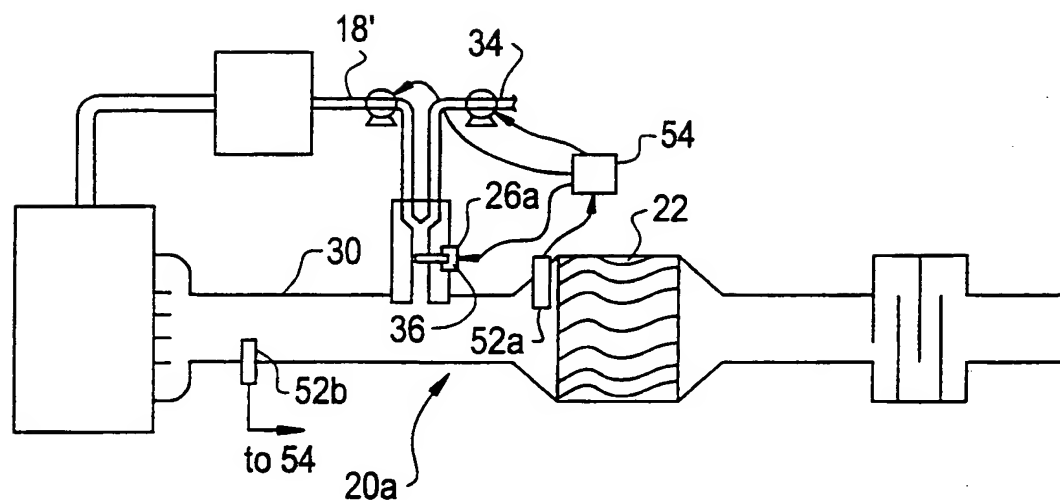
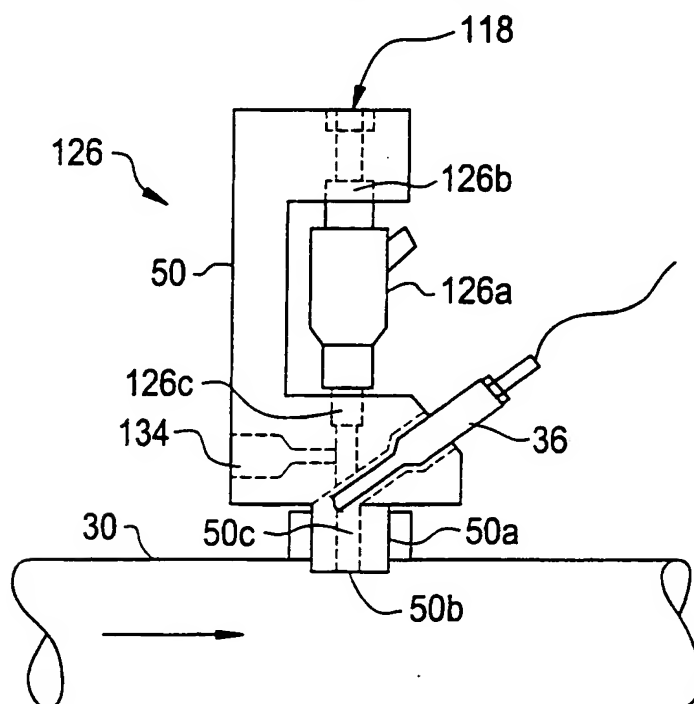
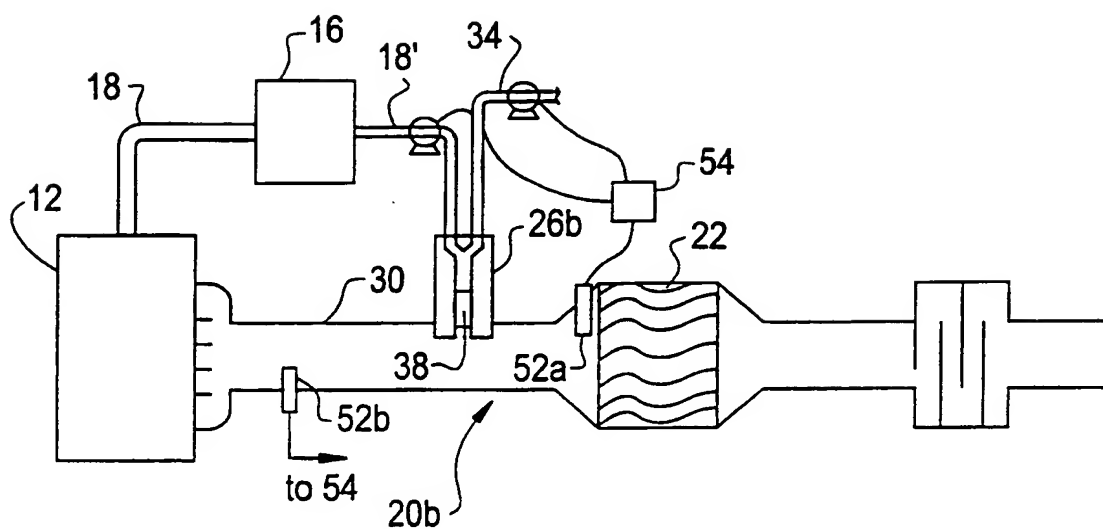


FIG. 5B



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FIG. 6



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FIG. 7A

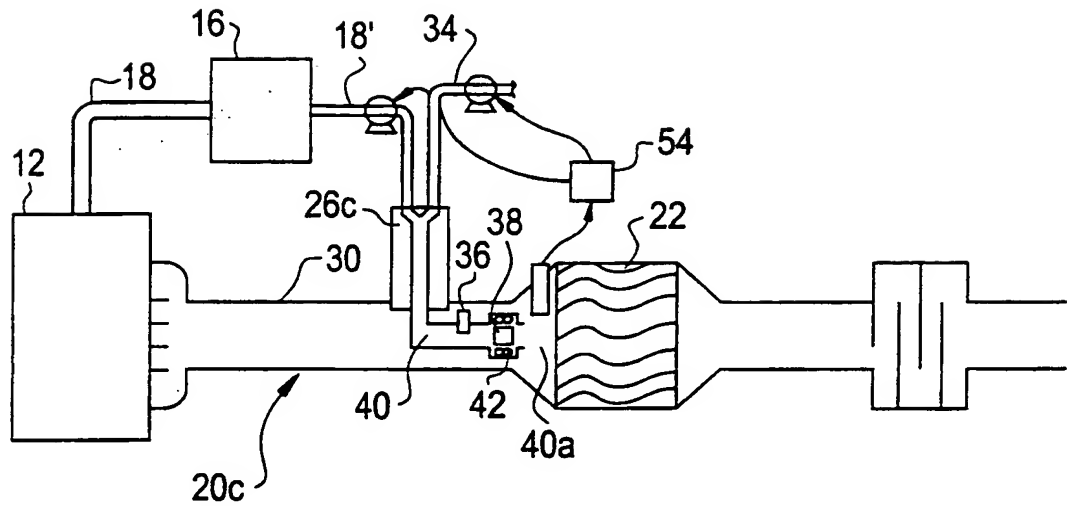
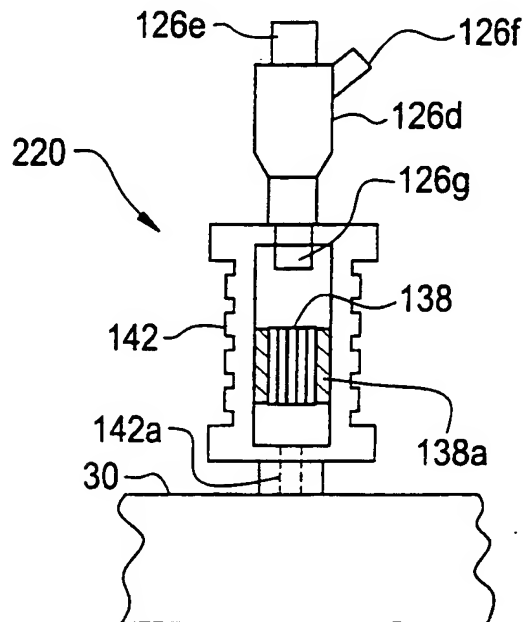


FIG. 7B



INTERNATIONAL SEARCH REPORT

Int lonal Application No
PCT/US 00/30507

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 F01N3/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 586 433 A (WEISWEILER WERNER ET AL) 24 December 1996 (1996-12-24)	1-3,5, 13,16, 19, 21-23, 31,34, 37-51
A	the whole document	24,55,57
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 579 (M-1698), 7 November 1994 (1994-11-07) -& JP 06 212952 A (MITSUBISHI MOTORS CORP), 2 August 1994 (1994-08-02)	1-3,13, 16,19, 21,22, 31,34, 37-39, 41, 43-45, 49,51
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Int lonal Application No
PCT/US 00/30507

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A	column 7, line 19 - line 52; figure 6	5, 23, 49, 51, 55, 57
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A	abstract page 5, last paragraph -page 7, paragraph 2 page 11, paragraph 2 -page 12, paragraph 1 page 16, last paragraph -page 17, paragraph 1	2, 21, 22, 55, 57
X, P	EP 0 971 102 A (MITSUBISHI MOTORS CORP) 12 January 2000 (2000-01-12)	1, 5, 8, 9, 13, 16, 37, 38, 40, 43, 44, 46, 49, 50
A	abstract column 4, line 22 -column 7, line 45; figure 1	2, 11, 14, 17, 19, 21-23, 26, 27, 29, 31, 32, 34, 35, 55, 57
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	<p>PATENT ABSTRACTS OF JAPAN vol. 018, no. 389 (M-1642), 21 July 1994 (1994-07-21) -& JP 06 108825 A (MITSUBISHI MOTORS CORP), 19 April 1994 (1994-04-19) cited in the application</p> <p>abstract; figure 1 -& DATABASE WPI Section Ch, Week 199420 Derwent Publications Ltd., London, GB; Class E36, AN 1994-164561 XP002161899 abstract</p> <p style="text-align: center;">---</p>	<p>1,2,5, 19, 21-23, 37-39, 43-45, 49,51, 55,57</p>
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